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OCTOBER 28, 1940
VOLUME 29, No. 22

AMERICAN DYESTUFF REPORTER

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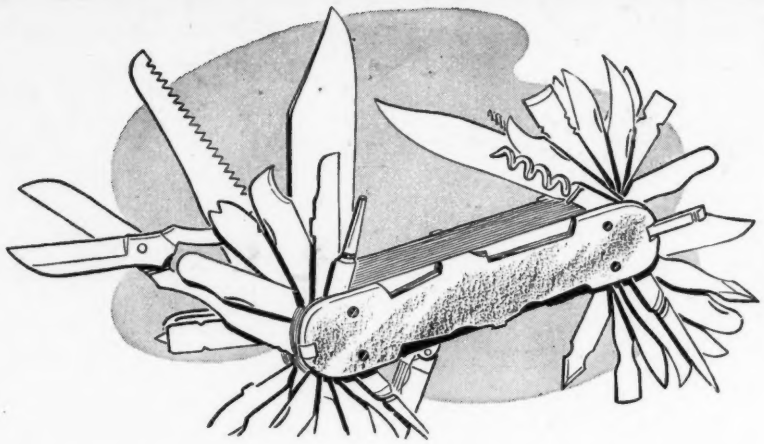

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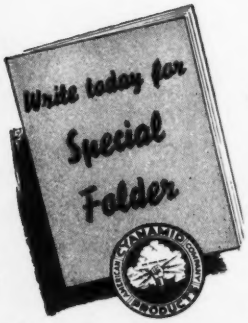

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Contents

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

• Special Articles

The Phenomenon of Fluorescence..... 579
Henry E. Millson

Reaction of Silk Fibroin with Diazomethane..... 583
Henry A. Rutherford, Wilbur I. Patterson and Milton Harris

A Comparison of Carbon Tetrachloride, Naphtha, and Water for the Cleaning of Cellulose-Acetate Rayon, Regenerated-Cellulose Rayon, Wool, Wild Silk, Silk and Weighted Silks 599
Florence Barr, A. J. Marshall and Rachel Edgar

• Departments

Trade Notes—New Products..... 604

• Proceedings of the American Association of Textile Chemists and Colorists

Calendar of Coming Events..... P587

Applicants for Membership..... P587

The Development of Methods for Determining the Causes of Damage Appearing in Wool Cloth After Dyeing P588
B. A. Ryberg

Twentieth Annual Meeting and Convention..... P593

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AMERICAN
DYESTUFF REPORTER

VOLUME 29 OCTOBER 28, 1940 NUMBER 22

The Phenomenon of Fluorescence*

HENRY E. MILLSON**

I

ALL scientists are agreed upon one point in connection with light, i.e., that it is some form of energy, probably electromagnetic in nature. Under this accepted theory, we must consider light in its broadest sense as including not only that which is visible to the eye but all energy radiated in the form of ether vibrations. Light travels in waves at the uniform velocity of 186,000 miles per second, but the waves vary greatly in length. Hence we have the obvious fact that the shorter the waves, the greater number of vibrations per second. Conversely, the longer the waves, the fewer vibrations per second.

The length of the light waves comprising the known spectrum is generally expressed in Angstrom units or A.U. An-Angstrom unit is one ten millionth of a millimeter and a millimeter is about one twenty-fifth of an inch in length. The human eye is able to receive and record only those rays falling between the narrow limits of about 4,000 and 8,000 Angstrom units and we call this the visible spectrum. The visible rays form a very small segment of the electromagnetic spectrum.

II

To explain the different radiations in greater detail there follows a separate paragraph for each type, starting with the longest or Hertzian waves and progressing through the ether spectrum to the shortest or cosmic rays.

Hertzian Waves

Radio and wireless waves fall in this class. Radio short waves are true waves of light and are used by physicians in giving therapeutic treatments.

Infra-Red

The infra-red rays lie beyond the red end of the visible spectrum. These rays are vibrating too slowly for the eye to see and are perceptible to us as heat through the sense organs in our skin.

Visible Light

This has been described above.

Ultra-Violet Rays

Since the ultra-violet radiations are of the greatest importance in fluorescence these rays and their effects will be described in detail later.

X-Rays

Next to ultra-violet on the short wave end of the spectrum we have the X-rays and their main use will immediately be called to mind, i.e., for taking pictures of the various organs and bones in the body and in the treatment of diseases.

Examination of fluorescent dyes for wool, cotton, rayon, silk and acetate under X-rays from an ordinary, small X-ray lamp failed to show any fluorescence whatsoever.

Gamma Rays or Radium Emanations

The gamma rays are produced when radium and other less radioactive elements such as thorium, uranium etc., transmute or change to other elements. The gamma rays have much greater penetrating power than X-rays. While pure radium is not luminous, when it is impure or mixed with other compounds, it gives off light and heat at an exact rate.

The light produced by radium is different in nature from fluorescence or phosphorescence caused by ultra-violet light. The radioactivity of radium is an atomic property and is a result of the disintegration of the atom. The light produced is therefore continuous and does not require any activating or exciting outside force for its development.

Cosmic Rays

The cosmic rays are the shortest known and are believed by some to come from far beyond the Milky way. These rays can shatter atoms and separate them into their various parts.

III

Having covered briefly the ether spectrum we are now in a position to consider the phenomena of iridescence and phosphorescence which are sometimes (probably inadvisedly) regarded as types of fluorescence.

Iridescence

Iridescence is the brilliant play of interference colors

*This is an abstract of Technical Service Bulletin No. 571.

**Technical Service Dept., Calco Chemical Division, American Cyanamid Company.

seen when visible light such as sunlight and incandescent light is reflected by certain bodies. Soap bubbles, oil films, etc., show this phenomenon. Iridescence that is visible to the naked eye and is developed without extraneous energy such as ultra-violet rays or X-rays, is not to be interpreted as fluorescence. In the phenomenon of iridescence there is no conversion of the ray length while in fluorescence there is a change of frequency, usually from a higher to a lower frequency.

Phosphorescence

Phosphorescence is the phenomenon of the re-emission of light by certain bodies which have the property of absorbing ultra-violet and other rays to which they are exposed and storing a portion of this energy, later to be given off again as a visible light. A distinction between phosphorescence and fluorescence is somewhat arbitrary. The criterion is based on the persistence of the emitted light. Most fluorescent compounds exhibit some phosphorescence, although of very short duration. Compounds should continue to glow for several seconds or longer after exposure to be considered phosphorescent.

Phosphorescence, it is believed, is caused by some such light rays as ultra-violet rays which build up excessive energy within the atom and force its electrons from one energy level to another. As these electrons return to their former energy levels, they release energy in the form of visible light. Application of heat or cold will accelerate or retard the phosphorescence. The light, however is equal to that for spontaneous emission, only the rate of decay being changed.

Dyes that are fluorescent when dyed on wool show no phosphorescence.

Fluorescence

Both organic and inorganic substances may exhibit fluorescence. All such compounds possess the property of absorbing invisible ultra-violet rays and converting them immediately into light which falls within the range of the visible spectrum. This ability to act as a transformer is characteristic of fluorescent materials. They differ mainly from phosphorescent compounds in that the fluorescent compounds cease to give off these lengthened light rays immediately upon the removal of the exciting force. This re-emission of light under the stimulating influence of the exciting radiation is called fluorescence. According to "Stokes' Law" the emitted light must have a longer wave length than that of the ultra-violet causing the fluorescence. A photon or quantum of light is emitted whenever the electrons change from a larger orbit to a smaller orbit within the atom or molecule.

Ultra-violet rays are invisible because the vibrations are too rapid and the wave lengths too short to impress the retina of the human eye. In the Angstrom scale, those waves which are shorter than 3,600 A.U. and longer than 136 A.U. constitute the ultra-violet radiations. The ultra-violet rays have much less penetrating power than the longer waves of white light for most substances. Thus ordinary window glass filters from the sunlight and daylight practically all of the very short and a considerable portion of the longer wave ultra-violet radiations.

IV
FLUORESCENT DYES

It has been shown by Toussaint that all synthetic organic coloring matters are more or less fluorescent. He found that the luminous emissions of greens and blues often fall in the infra-red region and are therefore outside the visible spectrum. Some fluorescent dyes in powder form do not fluoresce but when dissolved in water or other solvent or dyed on a fiber, they react to ultra-violet light. In dyeing fluorescent shades on wool, silk, rayon and other textile fibers, the intensity of the fluorescence increases as the shade becomes heavier until a maximum of brilliance is attained. This maximum is reached at different percentages depending upon the shade of each dye, its strength, purity of the bottom to which it is applied and other properties. From this peak the fluorescence gradually decreases, with increase in the percentage of dye used until, if carried far enough, very little if any fluorescence is obtained. Blacks, whether made entirely of fluorescent dyes or the usual chrome or acid types, do not show fluorescence.

Very light percentage dyeings show only slight or moderate fluorescence because of the relatively small number of fluorescent molecules absorbed by the fibers. Under ultra-violet light, these pastel shades often lack a distinct color tone and appear as a bluish, white glow.

In discussing fluorescent, moderately fluorescent and non-fluorescent dyes, there is considerable room for disagreement. Flourescence is subject to a certain amount of personal judgment. We do not all see a given shade the same in daylight, so it cannot be assumed that we would all read the colors of fluorescence alike. Therefore, some allowance must be made for this difference in the limits of our vision in making charts and statements. Considerable care has been taken to make the data presented here as accurate as possible. However, it is to be expected that others examining the same dyes in ultra-violet light generated by different lamps and passing through a wide range of filters will not agree entirely with the ratings of fluorescence in the lists to follow. Where lucid descriptions of what we see in ultra-violet light are difficult and sometimes impossible to make, a mere difference of terminology may make it appear that the statements are in disagreement with the facts. For this reason we must of necessity tolerate a wide latitude of opinions. Some dyes produce shades which are moderately bright when held within a few inches of a powerful source of ultra-violet light. If the shade is removed one or two feet from the lamp, it immediately becomes dull and no longer gives a distinct color tone. Such dyes may be construed as having a fluorescence but would not be suitable for the fluorescent design in a pattern. When judging the fluorescence of a dye, a standard such as Rhodamine B or Flavine should always be used for comparison. When examined alone, a dye with moderate fluorescence may appear bright, but when placed beside a sample having an excellent fluores-

cence, the one with moderate fluorescence often looks quite dull.

For textiles and decorative purposes, dyes, lacquers, and pigments must have the greatest brilliance possible in order to stand out from a dark background. In considering the suitability of a dye for textile purposes, it may be deemed satisfactory if it is bright when held at least ten feet from the light source.

A number of alizarine and milling blues and other dyes appear bright when dyed on bleached wool in ½ per cent strength and held close to an ultra-violet source. This apparent fluorescence may be caused in part by the blue-white fluorescence of the natural wool fiber.

The addition of non-fluorescent or even moderately fluorescent dyes to fluorescent dyes result in a very rapid diminution of the effect which is masked entirely in many cases. This quenching effect is probably due to the absorption of the converted light by the non-fluorescent dyes, which appear dull brown or black when exposed to ultra-violet rays. The fluorescing molecule of dye apparently transfers its increased energy to the non-fluorescent molecule with a resultant loss of brilliance.

For best results in dyeing or printing, the fiber should be as clean as possible. Yellow or dull stock causes a loss of fluorescence. White stock or a partially bleached bottom greatly improves the effectiveness of a shade under ultra-violet light.

Fluorescent dyeings on wool must be handled more carefully than regular acid shades. The condition of the dye in the fibers also determines the quality of the flouresence. If the dyes are precipitated on the outside of the fibers, due to the addition of too much acid or too rapid exhaustion of the dye bath, the brightness of the fluorescence will be reduced. The same dye when properly applied will be brilliantly fluorescent. Even when reasonable care is exercised fluorescent shades, especially on wool, do not reproduce accurately from batch to batch. The shades may be a good match in daylight and still fluoresce differently in ultra-violet light.

Fluorescent Carpets*

The use of ultra-violet in theaters for entertainment is well known but its use in moving picture theaters to prevent patrons from tripping and falling is entirely new. No doubt all of us have had the unpleasant experience of entering a theater from the bright sunlight and being practically blind in the apparent blackness. Theaters equipped with fluorescent carpet can now be absolutely dark and dyes in the carpet absorb the invisible ultra-violet radiations and change them to visible light. Thus the patron actually walks on a pathway of colored light generated within the fibers of the fluorescent carpet.

The main weakness of fluorescent dyes is their poor fastness to sunlight and daylight, but since theaters are always dark, this is not a serious drawback. Dry cleaning tests have been made of fluorescent wool shades with naphtha, carbon tetrachloride, benzol, gasoline, acetone, ethylene dichloride, sulfuric and petroleum ethers, and alcohol, and it was found that none of these agents affected the shade or fluorescence.

Shampooing tests caused the colors to run somewhat but they did not stain adjoining fibers. There was a loss of color body but the shades were more fluorescent after the treatment than before.

Walking on the carpet does not have any apparent detrimental effect on the fluorescence. The shades in fluorescent carpets can stand considerable soiling without any appreciable loss of brilliance under ultra-violet light.

*Use for this purpose covered by U. S. Patent No. 2,169,657

Other Fluorescent Dye Applications

There are fluorescent dyes available for nearly every kind of textile. At present the list includes wool, rayon, cotton, acetates, pure and tin weighted silk, nylon, linen and even synthetic casein fibers. In the case of cotton some direct, vat, azoic and sulfur dyes for fluorescent purposes may be had.

For leather there are numerous fluorescent dyes that are applied in the regular manner. Shellac or casein may be used as binders. In order to obtain a fluorescence of maximum brilliance and good coverage, an addition of barium sulfate should be made. Such finishes can be applied by swabbing or spraying.

Experiments have shown that lacquers containing fluorescent dyes will have good results. These lacquers can be made by dissolving cellulose nitrate, acetate, or ethyl cellulose in a suitable solvent and are used as a base or carrier. Fluorescent dyes may be added in a solution of water, alcohol, or carbitol.

The addition of barium sulfate thickens the lacquer, increases the smoothness and generally increases the brilliance of shade.

Fluorescent lacquers should be applied on a white or other light-colored base for best results. Black or dark bottoms greatly decrease the brilliance.

Plastics

There are also dyes for fluorescent effects in cellulose Ester Plastics. A range of colors are available for fluorescent coatings on paper by both the beater dyeing and the calender staining methods. A number of pigments have been found to fluoresce when ground in light varnish and than formulated into cellulose acetate lacquers.

(A complete list of Calco Fluorescent Dyes for all of the trades here is mentioned outlined in the bulletin. Tables giving the degree of fluorescence possessed by these dyes have been prepared and are included.)

V

SOME SOURCES OF ULTRA-VIOLET

Sunlight can be used if the solar radiations are first passed through a red-purple filter to exclude the visible rays. Tungsten and other incandescent bulbs will be satisfactory as a source of ultra-violet light provided a good filter is used.

The argon Lamp consumes 2½ watts, clear glass. It can be used in standard house sockets. No transformer is necessary. This is a cold form of bulb, gives some visible

light and ultra-violet light down to 3,100 A.U. The ultra-violet from this lamp will not cause sunburn or harm the eyes.

Several types of "black bulbs" are on the market and are of two main types, mercury vapor and photo flood filament; both require a red-purple filter of heat resisting glass. These give ultra-violet radiations from about 4,200 to 3,000 Angstrom units. Sperti is a high intensity mercury vapor type and generates considerable heat. The usual filter passes radiation of from 3,000 to 4,000 A.U.

NiCO is a mercury vapor type and is available in long tubes of special nickel-cobalt glass. These lamps give powerful ultra-violet rays down to about 3,200 A.U. This type of lamp is useful for mineral displays and home decorations.

Cold quartz lamps are useful for laboratory and mineralogical studies. These lamps give ultra-violet rays from 4,000 to 2,000 A.U.

Several types of carbon arcs can be used and require a heat resistant filter which in many cases is water cooled. The carbon arcs give a wide range of powerful ultra-violet rays which can be used for home and theater displays.

Filters For Ultra-Violet Lamps

The type of filter used determines to a considerable extent the quality and brilliance of the fluorescence obtained. Care must be exercised in using filters which pass considerable visible light that these red, blue or violet rays are not read as fluorescence.

A simple method for testing the presence of visible light is to use a book which has gold leaf letters printed on it. Under the H3 mercury vapor lamp, using a red-violet filter, these gold letters reflect a purple light when the book is held at certain angles. This is not due to fluorescence but is the reflection of the violet-red visible light which comes through the filter.

Short wave ultra-violet radiations will cause sunburn and would probably be fatal to us if we were exposed to them for a protracted period. They are also dangerous to the eyes and care must be exercised when working with ultra-violet below 3,200 Angstrom units.

VI

FADING COLORS WITH ULTRA-VIOLET

All artificial sunlight machines which are used for accelerated fading of dyed materials use ultra-violet for the purpose. Most machines have a carbon arc and moisture wicks to keep the humidity constant, while others use a mercury vapor tube.

When fluorescent shades are exposed to light, apparently a photochemical reaction takes place which reduces the fastness to light. Most organic fluorescent compounds, dyes, intermediates, etc., are quickly destroyed by light in the presence of air, oxygen, etc. This breaking down of such molecules with subsequent loss of fluorescence is probably due to an oxidation of portions of the fluorescent molecule. It may also be that the internal energy forces set up by the ultra-violet radiations may accelerate the destruction of the compounds in the presence of light.

Fading and its Effect on Fluorescence

When fluorescent shades are exposed to light, the fluorescent properties are generally destroyed in proportion to the fading of the color. This loss of fluorescence upon exposure to radiant energy is usually accompanied by a definite dulling of the shade.

A series of tests were made in strong sunlight during August and September to determine the types of visible rays most destructive to fluorescent materials. Colored and clear cellophanes were used as filters by stapling pieces on worsted flannel which had been dyed with fluorescent dyes. A few of those tested such as Calcomine Brilliant Flavine S, Calcocid Rhodamine 3B Conc., and Calco Eosine J have been discussed in the bulletin in detail. Other dyes reacted somewhat the same. None of the cellophanes used were fluorescent. The pieces were exposed for periods ranging from 9 to 30 hours and each had two sheets of red, orange, yellow, green, medium blue, dark violet, light violet, and clear cellophane. Transmission characteristics of all cellophanes used were checked spectrophotometrically.

In all cases the red afforded the greatest protection followed by orange, and dark violet, with yellow, green and light violet about the same. Medium blue and clear afforded the least protection. No fading of color was apparent in the red, orange, yellow, green, and dark violet cellophanes themselves. The light violet showed a slight loss of color and the medium blue considerable. This may account at least to some extent for the blue affording the least protection.

(A complete description of the results of these tests is available in the Bulletin.)

As might be expected no two of the fluorescent dyes tested reacted exactly alike with the same colored cellophanes. It was also noticed that the depth of color of the cellophane helped to protect the shade to some extent. However, these preliminary tests, though incomplete, indicate that the longer rays of the visible spectrum such as red (especially) orange, and yellow are less destructive to the fluorescence of a color than the shorter rays.

Though we have touched on only a few uses for ultra-violet, these examples give some idea of its potential possibilities. Even today we are using only a very small percentage of the energy that surrounds us. Without a doubt the future will see many new uses for these little-known rays. Just as Planck's quantum theory of radiant energy first described in 1900 made possible the use of the photo-electric cell for producing sound with motion pictures, and the long distance transmission of news pictures, so the discoveries of our physicists and chemists, though apparently unimportant today, may revolutionize the processes of the industries of tomorrow.

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Reaction of Silk Fibroin
with Diazomethane

HENRY A. RUTHERFORD, WILBUR I. PATTERSON and MILTON HARRIS*

ABSTRACT

The reactive groups in silk are intimately related to the absorption of moisture, acids, alkalies, or dyes, and to physical properties such as extensibility and tensile strength. A large proportion of these groups are present in silk fibroin in the form of hydroxyl groups of the amino acid tyrosine. The latter groups are of special interest, partly because of their preponderance, but principally because there are divergent views as to whether they are free in the untreated fibers. As an approach to the problem it appeared advisable to attempt to inactivate these groups by suitable chemical treatment and then to study the properties of the modified protein. Several methods have been tried for this purpose by different investigators but they were found to be too drastic, and generally resulted in severe physical deterioration of the fiber.

In the present investigation, the silk was treated with an ethereal solution of the methylating agent diazomethane. The treatment resulted in a rapid decrease in tyrosine content of the silk with no appreciable decrease in tensile strength of the fibers, and the results led to the conclusion that the hydroxyl groups of tyrosine are free in the untreated fibers. The total methoxyl content after treatment of the fiber for 25 hours or longer was greater than could be accounted for by assuming that only phenolic hydroxyl groups had reacted. The "extra" methoxyl was not on either the primary amino or the serine hydroxyl groups, but appears to have resulted from the reaction of diazomethane with groups, tentatively assumed to be carboxyl, to form the methyl esters.

I. INTRODUCTION

MANY of the chemical and physical properties of a protein are intimately related to the number and arrangement of its functional or reactive groups, most of which are contributed by the dibasic and diacidic amino acids. Silk fibroin is composed largely of the amino acids, glycine, alanine and tyrosine, and of these only the last one would be expected to contribute a reactive group, namely, a phenolic hydroxyl group. This group thus becomes of special interest.

As the result of observations in this laboratory, it appeared that the hydroxyl groups of tyrosine might not be free in the untreated fiber. For example, it was found that when fibroin was treated at pH 8 with Folin's phosphomolybdate phenol reagent[1], only a pale blue color, indicative of phenolic hydroxyl groups, was produced, but as the pH was increased the solution became increasingly colored. Pretreatment of the silk with alkali also increased the depth of color obtained with this reagent. Similar results were obtained with other proteins (pepsin and wool) and it appeared that not all of the phenolic hydroxyl groups of these proteins were free. Further evidence favoring this view was obtained by Fruton and Lavin[2] who observed that the characteristic absorption bands of tyrosine were not found in untreated papain, although on acid hydrolysis appreciable amounts of the amino acid were liberated.

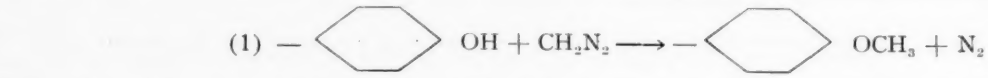
The state of this hydroxyl group in the silk fiber becomes of considerable importance, since it would be expected to influence such properties of the fiber as tensile strength, extensibility, and absorption of moisture, acids, alkalies or dyes. Unfortunately, the experiments indicating that the hydroxyl groups are not free must be considered inconclusive, and open to some criticism since they involve the use of treatments which are known to have a degradative effect on the protein. It appeared that a better approach to the problem might be made by attempting to cause the hydroxyl group to react with suitable mild chemical reagents under conditions which would minimize the possibility of degradation of the fibers.

Of the available reagents, the acid chlorides or anhydrides, ketene, and diazomethane appear to be most suitable for inactivating the hydroxyl groups of tyrosine. The acid chlorides and anhydrides were used for this purpose by Abderhalden and Brockmann[3, 4], but were found to produce appreciable deterioration of the fibers. Ketene was used by Kise and Carr[5, 6] with far more satisfactory results, although on prolonged treatment with this reagent, the fiber was colored tan and some degradation occurred. The product of the reaction of ketene with the hydroxyl group of tyrosine is an ester which is readily hydrolyzed in either alkaline or acid solutions. For this reason, it is not possible, by the usual tyrosine analyses, to estimate quantitatively the extent to which the ketene has reacted with the hydroxyl groups. Further, the acetyl value of the treated fiber is also inadequate for this purpose since it is known that the ketene reacts with groups other than the phenolic hydroxyl group.

Daizomethane offers several advantages over the abovementioned reagents. It can be used in neutral aqueous

*Research Associates at the National Bureau of Standards representing the Textile Foundation, Inc.

or organic solutions and it reacts with a phenolic hydroxyl group to form an ether as follows:



The product of the reaction is stable during the alkaline hydrolysis used in tyrosine determinations, which makes possible the quantitative estimation of the extent to which the tyrosine has reacted. The reagent was used by Herzig and Landsteiner[7], and by Abderhalden and Brockmann[8] on several proteins including silk but the extent of the reaction with tyrosine was not determined. The methoxyl contents of the treated fibers, however, were found to be greater than would be expected if only the phenolic hydroxyl groups were reacting.

II. EXPERIMENTAL PROCEDURE

1. Materials and Methods

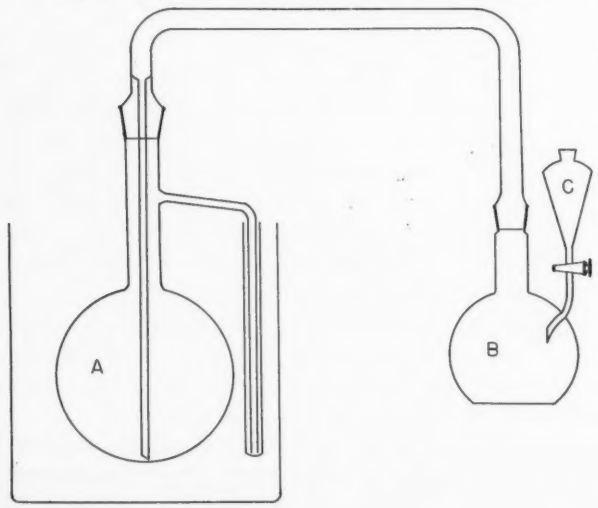
Silk fibroin in the form of a plain-woven cloth was used in this work. Before treatment with diazomethane it was extracted for 8 hours each with alcohol and with ether, and finally washed thoroughly with cold distilled water.

Total nitrogen was determined by the micro-Kjeldahl method, tyrosine by Lugg's method[8] after an alkaline hydrolysis, amino nitrogen by the method of Rutherford, Harris, and Smith[9], methoxyl content by the procedure described by Vieböck and Brecher[10], and methyl alcohol by Beyer's method[11].

2. Preparation of Diazomethane

The ethereal solution of diazomethane was prepared according to the method described by Adamson and Kenner[12]. The apparatus is shown in Figure 1. The temperature of the reaction flask B was maintained at 75° to 80° C. in a water bath, and that of the receiver A at —10° to —15° in a brine tank. Before the distillation of the diazomethane was started, about 100 ml. of ether was added to flask A, and 10 ml. to the trap at the side arm of A. 0.05-mole of the nitroso derivative of the methylamine addition product of mesityl oxide in 40 ml. of ether and 6 ml. of isopropanol was added dropwise from funnel C to 30 ml. of 1 per cent sodium isopropoxide in flask B, the rate of addition being slightly greater than that of distillation. When the addition was complete, 15 ml. more of 1 per cent sodium isopropoxide was added to B, followed by another 0.05-mole portion of the nitroso ketone as before. Finally, ether was added to flask B until all the diazomethane was distilled into A. By this procedure about 1 g. of diazomethane in 250-300 ml. of ether was obtained. The actual amount was readily determined by the addition of an aliquot of the ether solution to a weighed quantity of benzoic acid, and subsequent titration of the excess acid with 0.1 *N* potassium hydroxide in alcohol[15].

Fig. 1—Apparatus for preparation of diazomethane.



3. Methylation of Fibroin

Preliminary experiments showed that the rate of methylation of the tyrosine hydroxyl groups of the silk was increased by the presence of a little moisture, by increased concentrations of diazomethane, or by treating the fibers at low temperatures (—10° C. or below). On the basis of these experiments the following procedure was used. The sample was first wet thoroughly with 75-per cent alcohol and then squeezed as dry as possible. This wetting served to introduce an appreciable quantity of water into the fiber, and when the sample was treated by this procedure, the subsequent separation of a water layer in the ether solution was avoided. The silk was then placed in flask A containing the diazomethane, and the reaction allowed to proceed at —10° to —15° C., for the desired length of time. A rapid rate of reaction was obtained when the ratio of diazomethane to silk was about 1:5. This is 4 to 5 times the amount required to completely methylate the fibroin. This concentration may be maintained approximately by distilling more diazomethane into flask A as the reaction proceeds. After the treatment, the silk was removed and the excess ether and diazomethane were allowed to evaporate. The samples were thoroughly washed in successive portions of distilled water to remove the remaining organic solvents and then allowed to dry.

III. RESULTS AND DISCUSSION

1. The Reaction of Silk with Diazomethane

The extent of methylation of the tyrosine hydroxyl groups of the silk was determined by analysis of the treated materials for tyrosine. The results in Table 1 show the tyrosine contents of samples treated for different lengths of time. The rate of reaction is quite rapid at

TABLE 1

Tyrosine and Methoxyl Contents of Silk Fibroin After Treatment for Different Lengths of Time with an Ethereal Solution of Diazomethane.

Duration of Treatment Hrs.	*Tyrosine Content %*	*Fibroin %*	*Methoxyl Content of Hydrolysate % Hydrolysate*	*Calc. from Decrease in Tyrosine Content %*
0	12.1	...	...	...
1	6.6	0.92	0.94	0.94
1.5	4.1	1.94	1.49	1.37
3	3.6	1.97	1.54	1.45
5	3.2	1.99	1.52	1.52
10	2.4	2.32	1.60	1.66
20	2.3	2.35	1.58	1.68
35	2.0	2.55	1.76	1.73
50	1.6	2.62	1.86	1.80

first and gradually decreases as the treatment is continued. In 10 hours, 80 per cent of the total tyrosine is converted into the methyl derivative. Treatments for longer periods of time, during which the concentration of diazomethane was kept nearly constant, resulted in a slight further decrease in tyrosine content. The rate of reaction may in part depend on penetration of the reagent into the fiber, and it might accordingly be expected that those groups on and near the surface would be methylated most rapidly. No appreciable decrease in tensile strength of the fibers occurred even on prolonged treatment. Since practically all of the tyrosine in silk is so readily methylated under these conditions, it appears that the hydroxyl groups of this amino acid are free in the untreated fiber.* A possible explanation of the discrepancy between this conclusion and that of the experiments with Folin's phenol reagent previously described might be found in a consideration of the nature of the reaction in the Folin method. This reaction depends on the oxidation of a phenolic hydroxyl group by the reagent, the latter in turn being reduced to the highly colored state. The depth of color developed by a known amount of tyrosine is used as a standard. If, however, the oxidation potential of the hydroxyl group of the tyrosine as it exists in the protein is different from that of the tyrosine itself, then the apparent tyrosine values obtained for the protein will not be true values. On this assumption, it would appear that the oxidation potential of the hydroxyl group is greater when the tyrosine is part of the protein molecule.

An examination of the data in columns 3 and 5 of Table 1 shows that the methoxyl content of the treated silk is greater than can be accounted for if it is assumed that only the hydroxyl groups of the tyrosine had reacted. Presumably, the "extra" methoxyl results from the reaction of diazomethane with other groups in the fiber. Conceivably, diazomethane might react with silk in several ways, as shown in the following equations:

(1) $P—CH_2—C_6H_4OH + CH_2N_2 \rightarrow P—CH_2C_6H_4OCH_3 + N_2$

(2) $P—CH_2NH_2 + CH_2N_2 \rightarrow P—CH_2NHCH_3 + N_2$

(3) $P—CH_2COOH + CH_2N_2 \rightarrow P—CH_2COOCH_3 + N_2$

(4) $P—CH_2OH + CH_2N_2 \rightarrow P—CH_2OCH_3 + N_2$

where, P represents the protein molecule to which the above groups are attached. The equations then represent the reaction of diazomethane with (1) the hydroxyl groups of tyrosine, (2) the free amino groups, (3) the free carboxyl groups, and (4) the hydroxyl groups of serine.

Reaction (1) is shown to occur by the decrease in tyrosine content of the treated silk. Reaction (2) would result in the formation of a methylamino compound which would not give methoxyl under the analytical conditions used, and would therefore not account for any "extra" methoxyl. Moreover, amino-nitrogen determinations as shown in Table 2, indicate that this reaction does not occur. Reaction (3) undoubtedly occurs since diazomethane is known to readily methylate carboxylic acids with the formation of methyl esters. Upon hydrolysis of the fibers under the conditions generally used in the tyrosine determination (6 *N* NaOH for 20 hours at 105° C.) such esters would be expected to decompose liberating methyl alcohol with the regeneration of the carboxylic acid. The former would be evolved, and thus the methoxyl content of the hydrolysate should represent those methoxyl groups which resist the hydrolytic conditions used in these experiments. Reactions (1) and (4) would give this type of methoxyl.

TABLE 2

Total and Amino-Nitrogen Contents of Silk After Treatment for Different Lengths of Time wtih Diazomethane.

Duration of Treatment Hrs.	*Total N %*	*Amino N %*
0 (untreated)	18.78	0.10
20	18.82*	0.10
50	18.81*	0.10

*Corrected for increase in weight due to the addition of methyl groups.

The methoxyl contents of the hydrolysates are shown in the fourth column of Table 1. As was expected, the values are lower than those obtained for the treated silk (column 3). The agreement of the hydrolysate values with the methoxyl values calculated from the decrease in tyrosine contents (column 5), however, leaves little likelihood that reaction (4) occurs to any appreciable extent, especially since complete methylation of the serine of silk (1.8 per cent[13]) would yield 0.53 per cent of methoxyl groups or about 30 per cent of the total found.

The liberation of methyl alcohol from methylated silk during hydrolysis was readily demonstrated by refluxing several different samples for 1 hour with 0.1 *N* NaOH, and then distilling about half the solution into a receiver maintained at 0° C. (to avoid loss of CH_3OH). The methyl alcohol content of the distillate was determined colorimetrically by Beyer's method. The results, calculated as methoxyl, are shown in Table 3.

If it is tentatively assumed that the "extra" methoxyl in the treated silk is in the form of esterified carboxyl

*It is of interest to note that the tyrosine contents of silk sericin, crystalline pepsin, and wool were reduced from 6.3, 7.8 and 5.8 per cent to 0.5, 1.8, and 1.4 per cent respectively after treatment for 20 hours with diazomethane.

TABLE 3
The Effect of a 1 Hour Treatment with a Boiling 0.1 *N* Solution of Sodium Hydroxide on the Methoxyl Content of Methylated silk.

Duration of Diazomethane Treatment Hrs.	*Total Methoxyl Content* %	*Methoxyl Liberated During Hydrolysis as Methyl Alcohol* %	*Residual Methoxyl Content of Silk* %
3	1.97	0.30	1.55
10	2.32	0.50	1.85
50	2.62	0.73	2.08

groups, the present results indicate that silk fibroin contains an appreciable quantity of dicarboxylic amino acids, though this seems not to have been reported in the literature. From the data in Table 1, it is estimated on the basis of the above assumption, that silk may contain as much as 0.26 millimole per gram of free acidic groups. Such an appreciable amount of acidic groups would be expected to considerably influence the acidic and basic properties of the silk, and should be readily detectable in the titration curve of the fiber.*

During these studies it was observed that an appreciable quantity of alkali was liberated when the fibroin was washed with water subsequent to the diazomethane treatment. A possible explanation for this is that cations, held by the acidic groups of the fiber, are freed as these groups react with diazomethane. Since the reaction was carried out in ethereal solution, the alkali was not removed from the fibers until they were washed with water. If such an explanation is correct, no alkali should be liberated from ash-free silk under similar conditions. Furthermore, the rate of reaction of ash-free silk with diazomethane might be very different than that of the untreated silk since at least a portion of the acidic groups of the latter would already be combined with inorganic substances.

In order to test this explanation and its consequences, a sample of ash-free fibroin was prepared by electrodialysis and then treated with diazomethane for different lengths of time. It was found that no measurable quantity of alkali was liberated when the treated sample was washed with water. Furthermore, the rate of increase in methoxyl

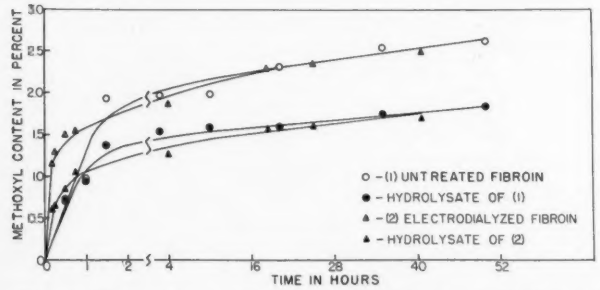

METHOXYL CONTENT IN PERCENT
TIME IN HOURS
○ - (1) UNTREATED FIBROIN
● - HYDROLYSATE OF (1)
▲ - (2) ELECTRODIALYZED FIBROIN
▲ - HYDROLYSATE OF (2)

Fig. 2—Rate of reaction of untreated and electrodialyzed fibroin with diazomethane.

content of the electrodialyzed silk during the first hour of treatment was greater than that of the untreated fibers as shown by the results plotted in Figure 2. After one hour of treatment no "extra" methoxyl was found in the latter while treatment of the electrodialyzed fibers for the same length of time resulted in the formation of about 65 per cent of the maximum "extra" methoxyl. After about 20 hours, there was no further increase in "extra" methoxyl content. As in the case of the untreated silk, the difference between the total and hydrolysate methoxyl contents of the electrodialyzed sample becomes approximately constant and equal to about 0.26 millimole per gram.

Although no further work on this phase of the investigation has been done, it appears from the rate studies that the specificity of diazomethane for the hydroxyl groups of tyrosine might be increased by appropriate pretreatment of the protein with some inorganic substance for the purpose of blocking the carboxyl groups.

2. Reaction of Methylated Silk with Nitrous Acid

The methylated and untreated samples of silk were found to behave quite differently toward nitrous acid. The untreated silk assumed the usual dark brown color, while the depth of color formed in the diazomethane-treated sample appeared to be dependent on the extent of methylation. A sample in which the tyrosine content had been reduced to a very low value was colored only slightly by nitrous acid.

Philpot and Small[14] have suggested that the color resulting from the reaction of pepsin with nitrous acid may be due to a nitrosation of the tyrosine, and that the first product of the reaction is an ortho-nitroso derivative. Assuming a similar reaction for silk, it appears that the methylation of the tyrosine prevents the formation of this derivative, either by decreasing the reactivity of the ortho position, or by preventing reaction of the nitrous acid with the free hydroxyl group to form a compound which subsequently rearranges to the ortho position. Regardless of which of the above mechanisms prevails, the difference in the behavior of methylated and untreated silks toward nitrous acid may be considered additional evidence that hydroxyl groups of the tyrosine in untreated silk are free.

*The titration curve of silk is now being determined as part of a separate investigation in progress in this laboratory.

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Complete Reports of the Twentieth Annual Meeting and Convention of the A.A.T.C.C. Will Appear Shortly

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The Development of Methods for Determining the Causes of

Damage Appearing in Wool Cloth

After Dyeing

B. A. RYBERG*

THE problem of damaged wool occurring before and during manufacture is a very real one. It has been conservatively estimated to cause a loss of 3-5 per cent of the value of the output of the woolen and worsted industry. It, therefore, presents a very important field for research and any useful information obtained by such research would be of great value.

This field has not been overlooked by any manner of means, as can be attested to by the number of publications relating to this particular field. However, the amount of useful information to be found in these publications is very small and in practically all cases, deals with the detection of damage on undyed material. There appear to be a few methods for detecting damage quantitatively but none of them indicate the cause of the damage with any degree of certainty. They depend mostly on color reactions which are of little use on dyed material. The dyeing process itself serves as a very sensitive method for detecting damage, but in most cases gives no indication of the cause of the damage. Since any damage which may exist is usually made evident in dyeing, methods for detecting damage are not as important as methods for determining the cause of the damage.

It is a fact that a fabric may be damaged, but if this damage is uniform and the fabric not unduly weakened, it is still a commercially acceptable fabric. This fact complicates the situation considerably since in most cases the wool is not recognized as being damaged unless the damage is noticed by the time the material reaches the finished state.

The number of agencies capable of producing damage in wool is considerable. In addition to these we have multiple damage produced by a succession of these agencies. The rough classification appearing at the top of the next column covers the majority of these agencies.

All methods developed for determining the cause of damage appearing in wool after dyeing, should be relatively simple and applicable in the average mill laboratory, to be of the greatest value.

The detection of damage in wool before it reaches the dyeing process is also important, since many troubles could be avoided or eliminated by so doing. M. Becke[1] uses the biuret reaction to determine the amount of wool substance which is dissolved by a given process, and a hot solution of stannous chloride plus acetic acid to determine alkali damage quantitatively. These methods are both based on color reactions.

Classification of Damage

Photo-Chemical	*Chemical*	*Mechanical*
Light damage resulting in Oxidation.	1. Light	Moth
	2. Bacteria	Friction
	3. Steam	Tension
	4. Water	Napping
	5 Heat (Dry)	Shearing
	6. Acid	Milling
	7. Alkali	Washing
	8. Oxidation (Bleaching)	
	9. Reduction (Stoving)	
	10. Sulfonation (Carbonizing)	
	11. Halogenation (Chlorination)	
	12. Metallic impurities	

Allwörden[2] proposes the use of chlorine water which causes damaged wool to swell more than normal wool, although Krais and Waentig[3] feel that bromine water gives better results. Sauers[4] method depends on the ratio of "soluble nitrogen" to total nitrogen, which varies considerably with the chemical treatment to which the wool has been subjected. Sieber's[5] newer method is based on the dyeing of tyrosine with alkaline diazo solution.

Krais and Schleber[6] advocate dyeing methods using e.g. Cotton Blue 10B, as being preferable to Nitrogen determinations and various color reactions of the breakdown products of wool, for proving alkali damage. Rimington[7] measures damage by means of Pauly's reagent, stating that his method is not applicable to dyed or naturally colored material, or when the degree of damage is small. Herzog[8] uses aqueous indigo carmine to detect damage in wool while Ristenpart and Schwerdtner[9] make use of Methylene Blue absorption as do Elmquist and Hartley[10], as a measure of the degree of deterioration.

Krais and Viertel[11] propose the use of an ammoniacal potash solution which causes acid damaged wool to swell, with subsequent formation and liberation of bubbles, to a much greater degree than undamaged wool. Krais, Markert and Viertel[12] feel that only absorption and swelling are suitable for the detection of very slight deterioration in wool, having checked all of the methods proposed by other investigators. Harris, Neville and Fritz[13] mention the Iodine Number of wool as a possible measure of chemical damage to wool, although McKay[14] states that the stoichiometrical relations found by Harris and his co-workers, between the iodine number and free amino nitrogen are shown to be of an accidental nature.

Schramek[15] in a study of wool damage caused by chemi-

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cals, found Allwörden's reaction, Methylene Blue absorption and the Markert, Krais, Viertel reaction to be either not sufficiently sensitive or are unsuitable for testing the action of alkali on wool and hair and give entirely contradictory results. The Pauli and Binz diazo reaction, he feels, is the only rapid method which gives sure indication of chemical damage.

Von Bergen[16] states that the effect of sunlight on wool can be determined by measuring the width of the fiber before and after swelling with caustic soda. King[17] proposes the use of indicators such as Thymol Blue, Phenol Red, Cresol Red, BromCresol Blue, etc., for detecting uneven distribution of acid or alkali in wool materials. Sieber[5] also uses a hot 1 per cent solution of benzopurpurine 10B which stains damaged wool but not undamaged wool. Elöd and Reuter[18] detect damage in wool by observing differences in the rate of absorption of an acid dye, damaged wool absorbing dye much faster than normal wool, particularly when alkali damaged.

Hirst[19] states that the action of wet steam or hot water increases the affinity of wool for dyes. Walde, Barr and Edgar[20] have shown that wool steamed in an autoclave for one hour at various pressures shows a progressive loss in strength with increasing pressure. A complete loss in strength is accompanied by a loss in nitrogen from 16.44 per cent to 15.72 per cent and sulfur from 3.88 per cent to 3.33 per cent. Fulton and Staniford[21] state that 12 pounds of steam for 10 minutes or atmospheric pressure for one hour does no damage to wool. Sixty pounds for 30 minutes makes wool friable. Astbury and Speakman[22] suggest that steam first attacks the side linkages of the keratin molecule.

Harris and Rutherford[23] propose a method for the detection of oxidation in wool by the use of a ferrous salt which is oxidized and then gives a red color with thiocyanate. Smith and Harris[24] use lead acetate to distinguish between untreated and hydrogen peroxide bleached wool. Again Smith and Harris[25] have shown that alkali solubility may be used as a measure of the extent to which wool has been oxidized.

Many of the methods proposed for detecting damage in wool are based on color reactions which are not applicable to dyed material; thus for dyed wool we are forced to rely on tests such as solubility and swelling in various reagents. If chemical methods of testing wool comparable to the Copper Number and Fluidity methods for determining damage to cotton and cellulose could be worked out, they would be of inestimable value.

The first step in our project after a survey of the literature[26], was to prepare a quantity of wool to be used as a basis for all of the work and which would be known as normal wool. This wool was prepared from a 62s Ohio Delaine wool, which was solvent degreased and thoroughly rinsed in warm water only. It was dry carded, dry combed and spun into a 2/16s low twist yarn suitable for use on a knitting machine. This yarn was then further prepared by extraction with ethyl ether followed by ethyl alcohol.

In beginning the active work it was deemed advisable to select only one or two types of damage for preliminary investigation, since greater progress could be expected than to attempt to carry on all simultaneously. Therefore, acid and alkali damage were selected for initial investigation, particularly since they are among the most prevalent types of damage.

Acid damaged and alkali damaged wool samples were prepared by treating wool in solutions of sulfuric acid of increasing concentrations at a boil for one hour, followed by thorough rinsing in water. A portion of each was neutralized with sodium bicarbonate and then rinsed thoroughly again (distilled water). The alkali damaged wool was prepared in much the same way using a temperature of 130°F. for one hour and sodium carbonate for the reagent. A portion of each was neutralized with acetic acid and rinsed in water.

Since our work is to be on dyed material ultimately, the use of color reactions for detection of the damage was automatically eliminated. We therefore turned to solubility tests.

Solubility of Damaged Wool in 0.2 N Sulfuric Acid

Samples of the acid and alkali damaged wools as well as normal wool, were treated in 0.2 N sulfuric acid at a boil for varying periods of time, then water rinsed thoroughly, neutralized in 2 per cent sodium bicarbonate solution, rinsed again and the loss in weight determined. The results (Figure 1) show a very definite difference in solubility between the acid and the alkali damaged wool, however, the magnitude of this difference is not great enough to be of much value as a test method, since a large degree of damage shows only a relatively small solubility. In the case of the acid damaged wool, the solubility appears to be directly related to the damage. In the case of the alkali damaged wool, increasing damage is accompanied by a much smaller change in solubility of a decreasing order.

The results obtained indicate that any test method based on the solubility of the damaged wool in dilute sulfuric acid would be of little use, due to its lack of sensitivity, therefore we have eliminated this method from our list of possibilities.

Solubility of Wool in Dilute Alkali Solutions as a Means for Differentiating Between Acid and Alkali Damage

The work of Harris and Smith[25] showing that alkali solubility may be used as a measure of the extent to which wool is oxidized, suggests that this method may also apply to types of damage other than oxidation. Harris uses 0.1N sodium hydroxide at 65°C. for one hour. The use of a constant temperature below a boil is usually not applicable to the average mill laboratory. Because of this fact it was decided to investigate other milder alkalies such as sodium carbonate, which might be used at a boil and still give approximately the same results as 0.1N sodium hydroxide at 65°C.

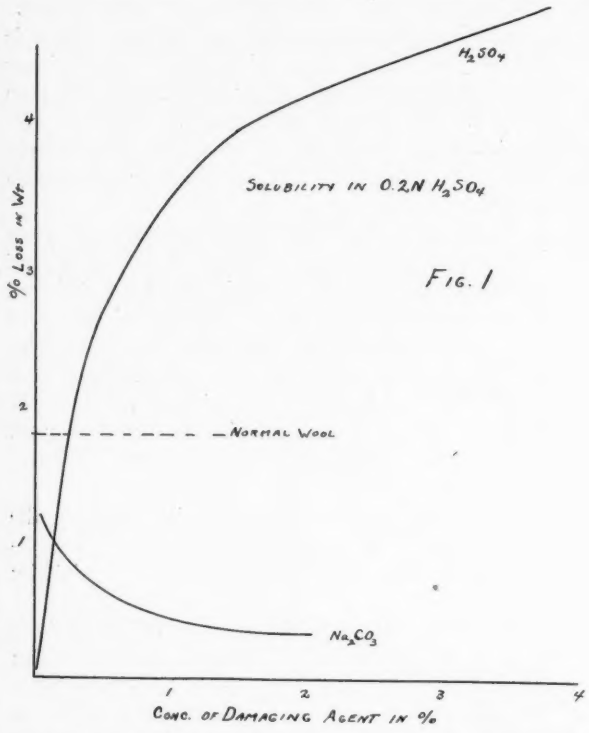


FIG. 1

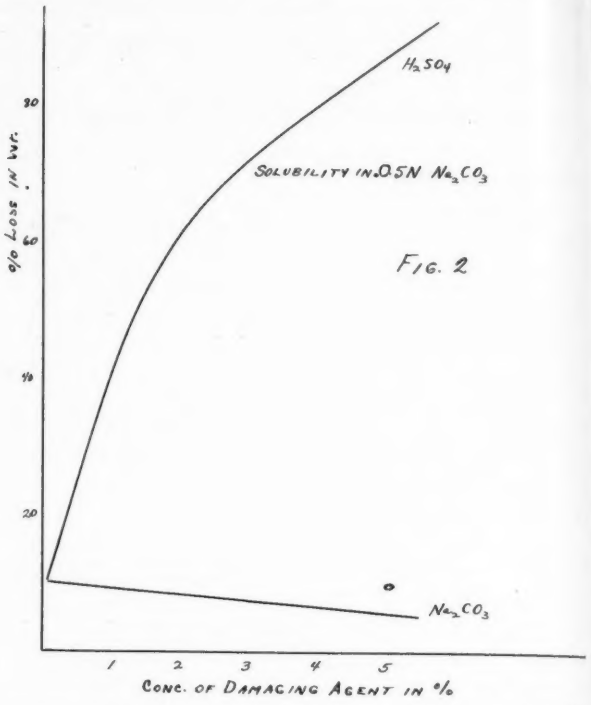


FIG. 2

Solutions of sodium carbonate of 0.1N, 0.05N and 0.02N were prepared and weighed* samples of the acid and alkali damaged wools were treated in 100X their weight of these solutions at a boil for varying periods of time. They were then rinsed in water, neutralized with dilute acetic acid and rinsed again, then dried and weighed.

In the case of 0.1 N carbonate solution, the time factor proved to be too critical, and with the 0.02 N solution the time necessary was too great for practical purposes. However, the 0.05N solution appeared to give satisfactory results. Normal undamaged wool loses approximately 10.0 per cent in weight when boiled for 30 minutes in 100X its weight of 0.05 N sodium carbonate solution. Acid damaged wool loses weight in direct relation to the degree of damage. Alkali damaged wool shows smaller losses in weight inversely to the degree of damage. Figure 2 shows the relationship between the degree of damage and the solubility in 0.05N sodium carbonate. The great difference in the alkali solubility of acid damaged as compared to that of alkali damaged wool is remarkable and this method appears to be much more indicative and useful than the solubility in dilute sulfuric acid, as a means for differentiating between acid and alkali damaged wool.

The great difference in the alkali solubilities of acid damaged and alkali damaged wools, suggested that this test should be applied to all of the known types of damaged wool, with the hope of dividing them into two or more groups, which, by other suitable tests (to be developed), might be further subdivided and eventually brought down to a single type of damage or at the most two or three.

*Samples were in duplicate, one being dried to constant weight, the other being taken as is. The oven drying to constant weight appeared to have little or no effect on the ultimate results.

Solubility of Wool in Dilute Alkali Solutions as a Means for Differentiating Between Types of Damage Other Than Acid and Alkali

Skeins of prepared wool yarn were damaged by light (Fadeometer), Carbonizing, Steam, Water, Dry Heat, Peroxide Bleaching and Chlorination. Their respective alkali solubilities were then determined using 0.05N Sodium Carbonate solution at a boil for 30 minutes. As a check on this method for determining alkali solubility, the more badly damaged samples were also tested by the method of Harris and Smith[25], using 0.1N Sodium Hydroxide solution for 1 hour at 65°C.

Results

Light Damage (Flannel in Fade-Ometer)

Fade-Ometer Hours	*Alkali .05N Na_2CO_3*	*Solubility .1N NaOH*
0	10.1%	10.8%
6	12.1	
12	13.7	
24	16.5	
48	17.9	21.8

Carbonizing Damage

Wool yarn was immersed in a 5 per cent solution of sulfuric acid at room temperature and worked for 15 minutes. A small amount of a wetting agent (naphthalene sulfonic acid) was added to ensure complete and uniform wetting out. The wool was thoroughly wrung out (clothes wringer) and then dried at 80°C. in moving air for 15 minutes. It was then baked 15 minutes at 125°C., thoroughly rinsed in

water, neutralized with ammonia, rinsed again and dried. The resulting yarn was badly tendered although of fairly good color.

Alkali Solubility

.05N Na_2CO_3	.1N NaOH
16.5%	19.7%

Steam Damage

Skeins of the prepared wool yarn were steamed at 15 pounds pressure (127° C.) for varying periods of time.

Alkali Solubility

Time in Mins.	.05N Na_2CO_3	.1N NaOH
0	10.5%	9.6%
6	10.7	
15	10.0	
30	10.7	
60	15.7	13.0

Water Damage

Skeins of the prepared yarn were heated in distilled water under 5 pounds pressure (108°C.) for varying periods of time, then wrung out and dried. (Domestic Pressure Cooker).

Alkali Solubility

Time in Hours	.05N Na_2CO_3	.1N NaOH
0	10.5%	9.6%
1	11.8	
2	12.4	
4	12.4	
8	13.8	13.8

Dry Heat Damage

Skeins of yarn were heated at 150°C. for 15 and 30 minutes, respectively in a laboratory drying oven.

Alkali Solubility

Time in Mins.	.05N Na_2CO_3	.1N NaOH
0	10.5%	9.6%
15	10.8	9.7
30 (badly yellowed)	12.1	11.9

Peroxide Bleach Damage

Skeins of the prepared yarn were treated in solutions of Hydrogen Peroxide of varying concentrations, all adjusted to a pH of 9.5 at 50°C., for 1 hour. They were washed, treated 15 minutes in a 1% bisulfite solution at room temperature and rinsed again.

Alkali Solubility

Conc. of H_2O_2 in Vols.	.05N Na_2CO_3	.1N NaOH
0	10.5%	9.6%
1	15.7	17.0
2	18.3	18.9
4	21.0	20.1
5	28.6	28.1

Chlorination Damage

Skeins of yarn were treated in Sodium Hypochlorite solutions of varying concentrations for 1 hour at 40°C., followed by an antichlor treatment with bisulfite.

Alkali Solubility

Conc. of H_2O_2 in Vols.	.05N Na_2CO_3	.1N NaOH
0	10.5%	9.6%
0.1%	17.3	
0.2	21.2	
0.4	28.0	
0.5	29.2	34.6

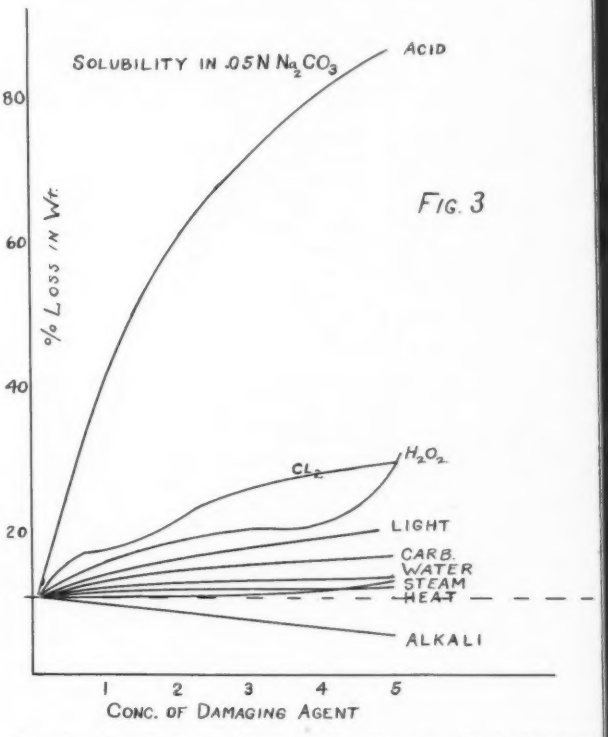
Wool damaged by 5 per cent sulfuric acid and 5 per cent sodium carbonate respectively were also tested by 0.1 N sodium hydroxide at 65°C.

Alkali Solubility

	.05N Na_2CO_3	.1N NaOH
5% H_2SO_4	75.0%	90.0%
5% Na_2CO_3	6.2	5.1

Where alkali solubility appears to be of a reasonable magnitude, sodium hydroxide appears to show greater differences than sodium carbonate, however these differences are comparatively small. Again Harris and Smith[25] have shown that reproducibility of analyses on untreated wool yarn are not very good, therefore sodium bicarbonate at a boil is as reliable as sodium hydroxide at 65°C.

The results of these tests indicate that the various types of wool damage can be separated into three groups by means of the alkali solubility test. Alkali damage should be readily detectable since it shows a decreasing alkali solubility with increasing damage, see Figure 3.



Classification of Wool Damage According to Alkali Solubility

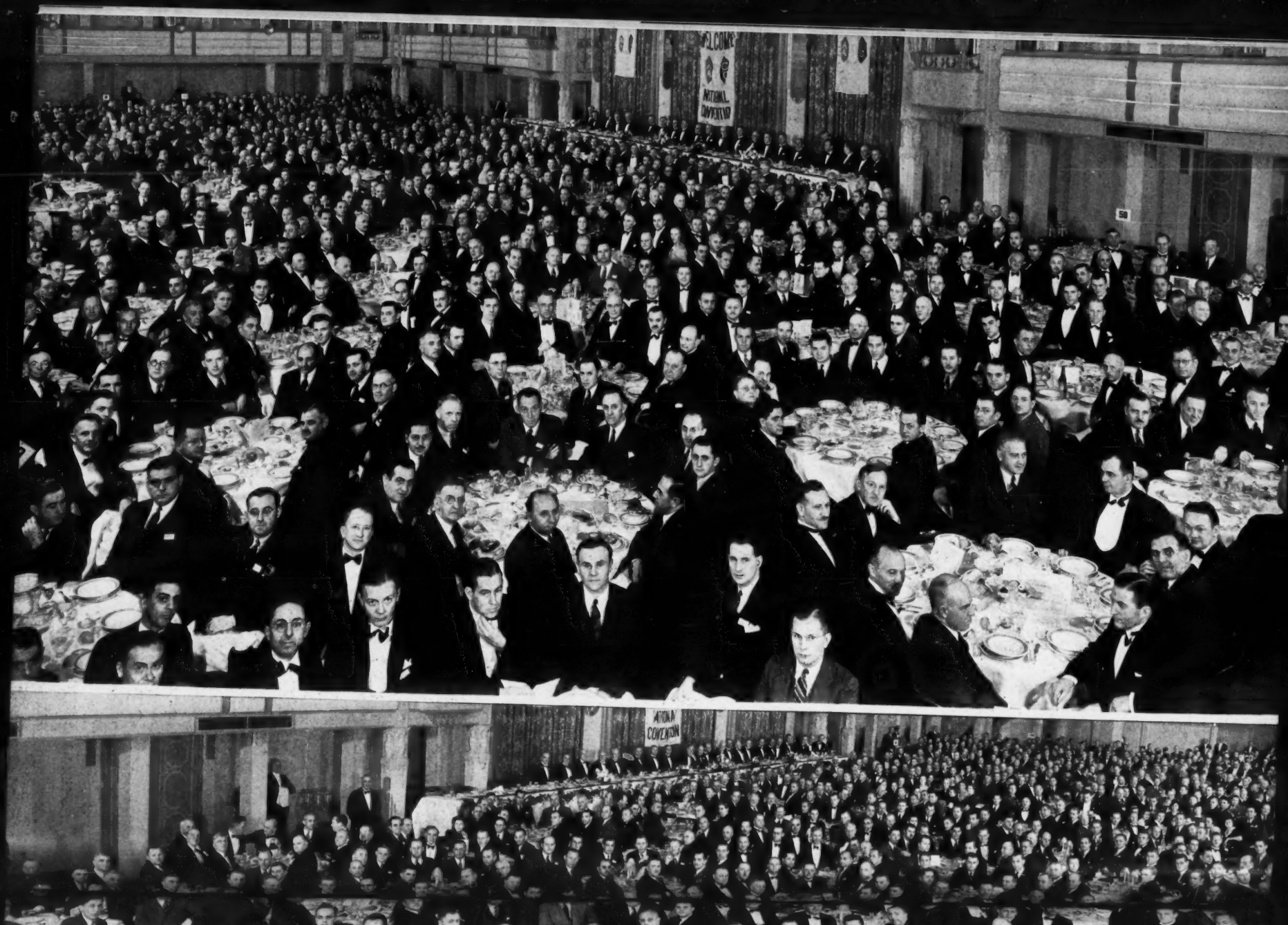
Lower Alk. Sol. than normal Wool	*Alk. Sol. of Normal Wool*	*Higher Alk. Sol. than normal Wool*
Alkali Damage	Steam Damage	Acid Damage
	Water Damage	Light Damage
	Dry Heat Damage	Carbonizing Damage
		Peroxide Damage
		Chlorination Damage

Another line of attack on this project deals with the swelling characteristics of wool under various conditions. Von Bergen[16] states that light damaged wool swells and curls more than uninjured fiber when treated with 0.1 N caustic soda. Swelling above 10 per cent may be taken as a proof of light damage and swelling of 100 per cent corresponds to complete destruction of valuable properties.

A Study of the Swelling Phenomenon of Wool When Treated with O.1 N Caustic Soda Solution

Individual fibers from normal wool, acid damaged wool and alkali damaged wool, were measured for width under

(Continued on page P595)


NATIONAL
CONVENTION

Two views of the large gathering which attended the twentieth Annual Banquet in the Grand Ballroom of the Hotel Commodore, New York City, October 19, 1940

Twentieth

ANNUAL MEETING AND CONVENTION

THE twentieth annual meeting and convention, held in New York City on October 18th, 19th and 20th, was one of the most successful in the history of the association. A well balanced program of technical papers, entertainment and nationally known speakers combined to make the occasion well worthwhile from every point of view.

Under the chairmanship of Dr. Walter M. Scott, the technical program proved to be exceptionally interesting. The intersectional contest on Friday afternoon and the two symposiums on Saturday morning proved their attractiveness and value by drawing overflow crowds to hear each paper. The intersectional contest proved to be so popular that it will probably be continued as a regular feature of the meetings.

The general arrangements committee, under the chairmanship of Patrick J. Kennedy, left nothing to be desired. The number who wished to attend the informal cabaret dinner and entertainment on Friday evening was so large that it was necessary to make arrangements to take care of the overflow crowd in another room. The grand ballroom of the Hotel Commodore was filled to capacity for the twentieth annual banquet on Saturday evening and the speakers were exceptionally well received by those in attendance.

On Sunday afternoon a luncheon was served at the National Advisory Committee's Building at the New York World's Fair. This was an unusually attractive building and no better choice could have been made.

The ladies who attended the convention were ably entertained by the chairman of the ladies' committee, Miss Bernice S. Bronner. A full program of events which was varied and unique was presented to them.

There appears in this issue photos taken at the luncheon of the research committee and council on Friday, the informal cabaret and dinner on Friday evening and the banquet on Saturday evening. In the next issue there will appear a number of informal snapshops taken around the hotel and at the luncheon at the World's Fair.

Future issues will also contain the technical papers, discussions and addresses.

The committees who were responsible for the success of this meeting are indeed to be congratulated upon the excellent quality of the program they arranged and which gave indication of the many months of hard work which preceded the affair.

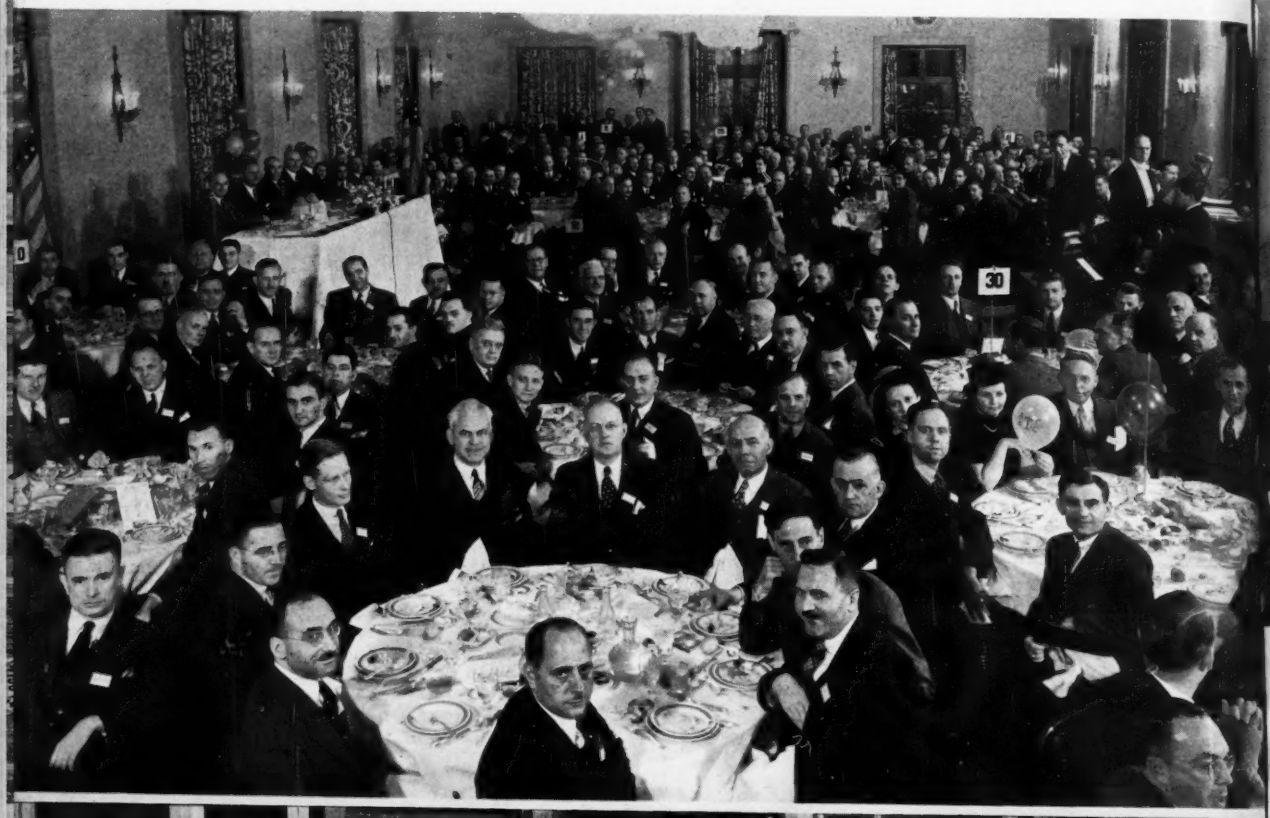
Awards for Sectional Contest Papers

At the luncheon at the World's Fair, Dr. Louis A. Olney, chairman of the committee of award on the sectional contest papers, announced the following winners:

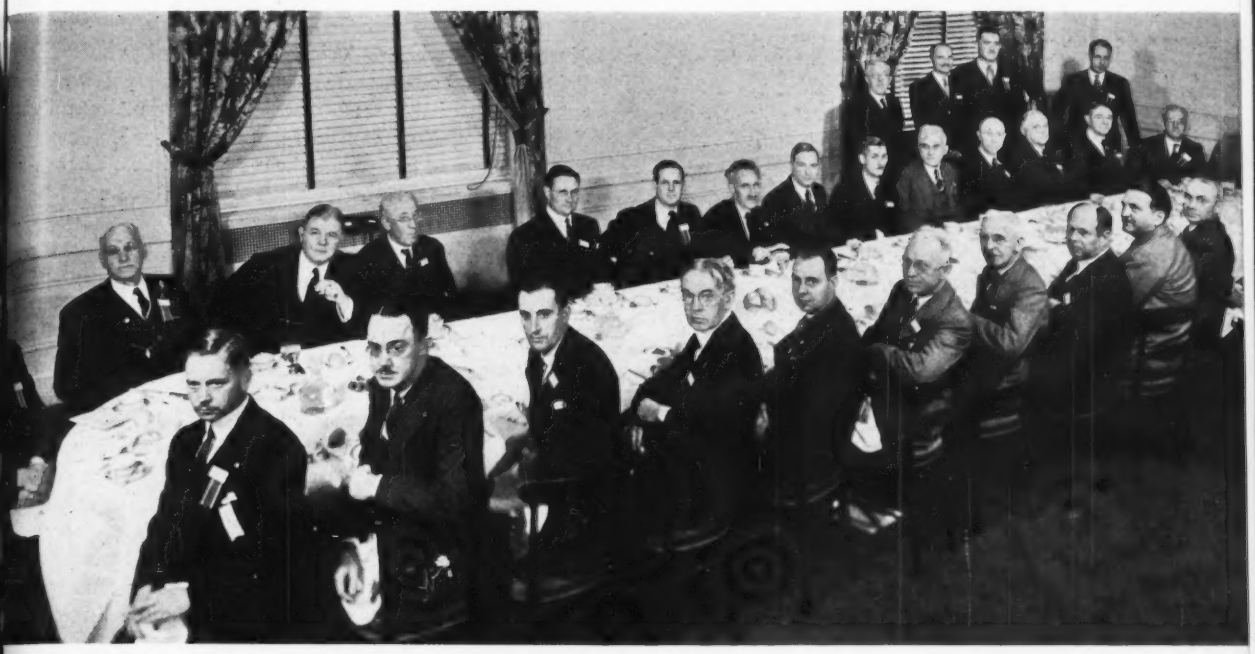
First—Rhode Island Section, "The Effect of Modern Finishing Agents on the Light Fastness of Cotton Colors," presented by William H. Cady.

Second—Southeastern Section, "Some Observations on the Tendering of Vat and Naphthol Dyed Army Duck on Total Exposure to Weathering," presented by A. R. Macormac.

Third—Philadelphia Section, "Variables Encountered in Fade-Ometer Testing," presented by C. A. Seibert.



Shown above are the two groups which enjoyed the informal cabaret dinner and entertainment at the twentieth Annual Meeting on Friday evening, October 18, 1940.



Luncheon for Council and Research Committee, Twentieth Annual Meeting and Convention, Hotel Commodore, New York City.

Damage Appearing in Wool Cloth

(Continued from page P591)

a microscope, using a disc micrometer. Each fiber was measured at five different points (minimum) and a minimum of 20 fibers of each type examined, was taken for measurement, so that the results for each type of damage was an average of not less than 100 individual measurements. These same fibers were measured dry, then remeasured after treatment with 0.1N sodium hydroxide solution.

The results obtained were very interesting (Figure 4) and the close relationship to the alkali solubility quite remarkable. However, since solubility is closely related to swelling, this is to be expected. An examination of the curves (Figures 2 and 4) show them to be almost identical.

The swelling characteristics of normal, acid damaged and alkali damaged wool when treated with other reagents known to be active swelling agents, were also determined. Sixty per cent formic acid shows such a small difference in swelling among the three types of damaged wool examined, as to make them indistinguishable, that is, within the experimental error. All three types of wool exhibited an increase of approximately 50 per cent in width when treated with the formic acid. It was observed during the course of these measurements that coarse fibers tend to swell more than fine fibers under the same conditions.

Fifty per cent mono-chloracetic acid exhibited practically the same swelling characteristics as the 60 per cent formic acid, it likewise showed little or no distinction between the various types of wool examined.

Fifty per cent tri-chloracetic acid gave substantially the same results as formic and mono-chloracetic acids, although of a slightly higher order, that is an increase of approximately 60 per cent in width, with no apparent distinction between the different types of wool tested.

Our results are in close agreement with those of Race, Rowe, Speakman and Vickerstaff[27], who have shown that light damaged wool can be uniformly dyed, when a high percentage of a swelling agent such as acetic acid is used. The report that increasing the swelling of the fibers as a whole tends to overcome the difference in swelling of exposed and unexposed wools.

The use of fluorescent dyes as possible specific indicators for damaged was suggested by several of the dyestuff manufacturers. A list of available fluorescent colors was obtained. They are:

Primuline	Color Index 812
Rhodamine B	Color Index 749
Rhodamine G	Color Index 752
Eosine Y	Color Index 768
Fluorescein	Color Index 766

The following dyes were also suggested*:

*A new colorless compound, Diazo Fast Yellow GGA, is now available and offers an opportunity for the use of a fluorescent substance on a previously dyed material.

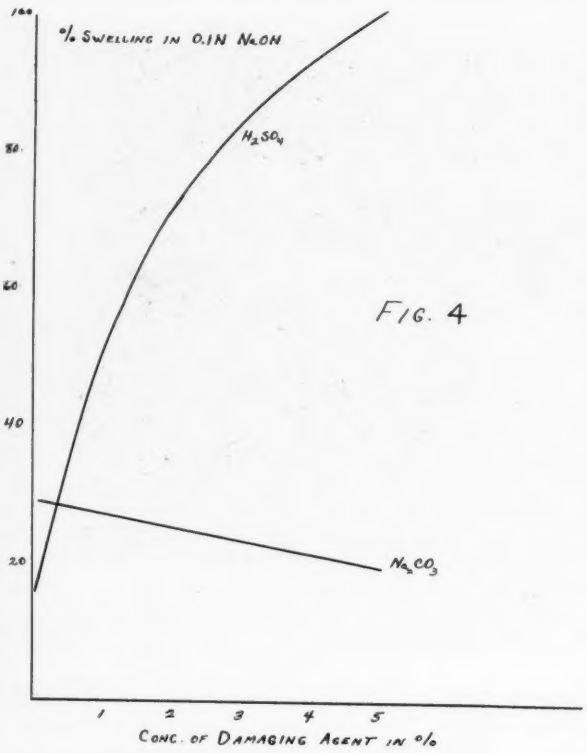


FIG. 4

Brilliant Sulfo Flavine FF.....Color Index
Formyl Violet S4B.....Color Index 698
Fast Acid Violet 10B.....Color Index 696
Chinoline Yellow Extra.....Color Index 801
Thioflavine TG .....Color Index 815
Phosphine Gn .....Color Index 793
Patent Phosphine .....Color Index 789

but these particular dyes upon examination, exhibited such a small degree of fluorescence that they were eliminated from further consideration.

Skeins of wool yarn damaged by the following agencies:

1. Alkali (2% Na_2CO_3, 1 hour at 55° C.)
2. Steam (1 hour at 15 lbs. or 127° C.)
3. Water (4 hours at 107° C.)
4. Heat (1 hour at 150° C.)
5. Acid (2% H_2SO_4, 1 hour at a boil)
6. Carbonized (5% H_2SO_4)
7. Peroxide Bleached (2.5 vol. H_2O_2 at pH 9.5)
8. Chlorinated (0.4% soln NaOCl)

were knitted alternately with normal wool to form a tube containing the above in stripes.

Several of the above tubes were dyed respectively with 1, Primuline; 2, Rhodomine B; 3, Eosine Y, by two different methods. Both methods were typical acid dyeings, using acetic acid and Glauber's salt, the main difference being that one was brought just to the boil while the other was boiled for one hour.

Primuline was absorbed much like a direct cotton dyestuff, Rhodamine like a basic dyestuff and Eosine like an acid dyestuff. The short dyeing method tends to show up differences in dye affinity due to damaged wool much better than a regulation dyeing. On the Primuline dyeing, Alkali, Steam, Water and Acid damaged wool appeared to take up more color than normal wool. Heated, Carbonized and Peroxide bleached wool were more nearly the shade of Normal wool, while Chlorine damaged wool was decidedly lighter than all others and brownish instead of yellow. Upon examination of this same piece under Ultra Violet light, Normal wool, Heat damaged and also Peroxide damaged wools, fluoresced fairly well, the rest very little. There was no greater difference under U.V. than under normal light between the various types of damage.

Another sample of normal wool which had been exposed to the Fadeometer for 48 hours, was also dyed with Primuline by both methods. The light damaged portions were much heavier in shade and under the U.V. the undamaged wool fluoresced fairly well, the damaged very little, but again the difference between damaged and normal wool was no more apparent than in daylight.

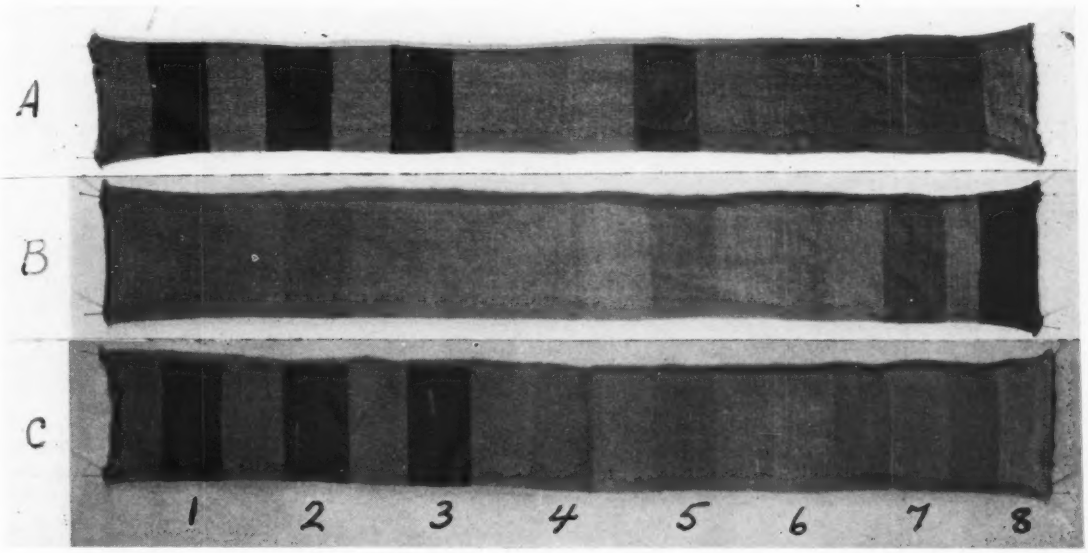
In the case of Rhodamine B, the greatest amount of color was absorbed by, Steam, Water damaged and Chlorine damaged wools; Acid and Alkali damaged wools took up somewhat less color than Normal wool, Heat damaged, Carbonizing and also Peroxide bleach damaged wools least of all. Again, under U.V. light the difference among the various types of damage was no greater than the differences to be seen under daylight.

The Eosine Y dyeing exhibited the deepest color on the Alkali, Steam and Water damaged wools. Acid damaged fiber appeared to have somewhat less color, and Normal wool, Heat damaged, Carbonizing, Peroxide bleach and Chlorine damaged wools were grouped more or less together, absorbing the least amount of color. Under U.V. light the same relationship exists and the difference in fluorescence between the various types of damage was not of a great enough magnitude to be of real use in distinguishing between types of damage, particularly on dyed goods.

Benzo Purpurine, Color Index 448, proposed by Sieber[5] was tried on the knit tubing and the short dyeing appeared to differentiate between some of the types of damage. (See Figure 5.) There was a rough separation into four groups. Group 1 containing Alkali damage, Water damage and Steam damage, appeared to absorb considerably more color than the others. Group 2 containing the Acid and Light damaged wools absorbed somewhat less color than Group 1. Group 3 containing Normal wool, Heat, Carbonized and Peroxide damaged wools with less color than Group 2 and Group 4 containing Chlorine damaged wool was much lighter in shade than all the others.

A short dyeing of Alizarine Saphirol B Color Index 1054, exhibited the same dyeing characteristics as the Benzo Purpurine.

A short dyeing with Methylene Blue Color Index 922, at pH 7 was made. Here Chlorinated wool absorbed much more color than any of the others. Peroxide bleached wool held somewhat less. Alkali treated wool still less and the others were only a little different from Normal wool, which was lighter than the Alkali damaged wool.



1, Alkali; 2, Steam; 3, Water; 4, Heat; 5, Acid; 6, Carbonized; 7, Peroxide; 8, Chlorinated.
A—Benzopurpurine B—Methylene Blue C—Alizarine Saphirole

Fig. 5

The possibility of using dyes such as Benzo Purpurine, Alizarine Saphirole B and Methylene Blue on dyed material, and measuring the dye absorption by means of a spectro photometer, may offer a means for differentiating between the various types of damage. It is hoped that such a possibility may be investigated.

The idea of stripping and redyeing damaged material with one of the above dyes has been proposed, but this merely introduces another factor of damage, which may so affect the others as to prevent their detection.

Beutel and Kutzelnigg[28] in their studies on keratins, postulated that during irradiation some of the sulfur in wool was converted to sulfide sulfur which readily reacted with lead acetate or other soluble lead salts. Assuming this to be true, it should be possible to detect light damage by determining the amount of sulfide sulfur in the suspected sample and comparing it with the amount obtained from a known undamaged sample, provided that light is the only agency of damage capable of producing appreciable amounts of sulfide sulfur.

The Effect of Lead Acetate Solutions of Varying pH on Normal and Damaged Wool

Skeins of the special prepared wool yarn were damaged as follows:

1. Alkali (2% Na_2CO_3 — 1 hr. 55° C.)
2. Steam (1 hr. at 15 lbs. or 127° C.)
3. Water (4 hrs. at 107° C.)
4. Heat (1 hr. at 150° C.)
5. Carbonizing (5% H_2SO_4)
6. Acid (2% H_2SO_4, 1 hr. at a boil)
7. Peroxide Bleaching (2.5 vol. H_2O_2, pH 9.5)
8. Chlorinating (0.4% soln NaOCl)

and then knitted alternately with normal wool to form a tube.

Several of the above tubes were treated in a 100X volume of 0.05 per cent solution of Lead Acetate at pHs varying from 2.5 to 7.0 at a boil for 40 minutes.

Results

Alkali, Steam and Water damage showed a darkening due to formation of Lead Sulfide, at all pHs but the contrast between normal wool and these was greatest at pH 4.4. Dry Heat and Acid damage exhibited a slight discoloration and Carbonized, Peroxide Bleached and Chlorinated parts show less color than normal wool.

Samples of wool cloth exposed to a Type FDA Fade-Ometer for 6-12-24 and 48 hours were also treated with lead acetate solution at varying pHs. In all cases a very noticeable formation of lead sulfide was found. The greatest difference between normal and light damaged wool was found to be at pH 4.4 as before*. (See Figure 6.) A comparison of light damage with alkali, steam and water damage showed that a small amount of light damage produced as much lead sulfide or more than a large amount of the other three types of damage. It is significant that pH 4.4 is also the iso-electric point of wool, the iso-electric point varying from pH 3.2 (Skinkle[29]), pH 3.4 (Harris[30]), pH 3.7 (Meunier and Ray[31]), through to pH 4.8 (Speakman and Stott[32]) and pH 5.8 (A. Wahl[33]).

Since our project is concerned with the identification of damage appearing after dyeing, a method must be found for determining the amount of sulfide sulfur formed by the action of light, which can be conducted on dyed material.

*Due to the difficulty of reproducing the results for this illustration, the ones shown may not substantiate the above statement.

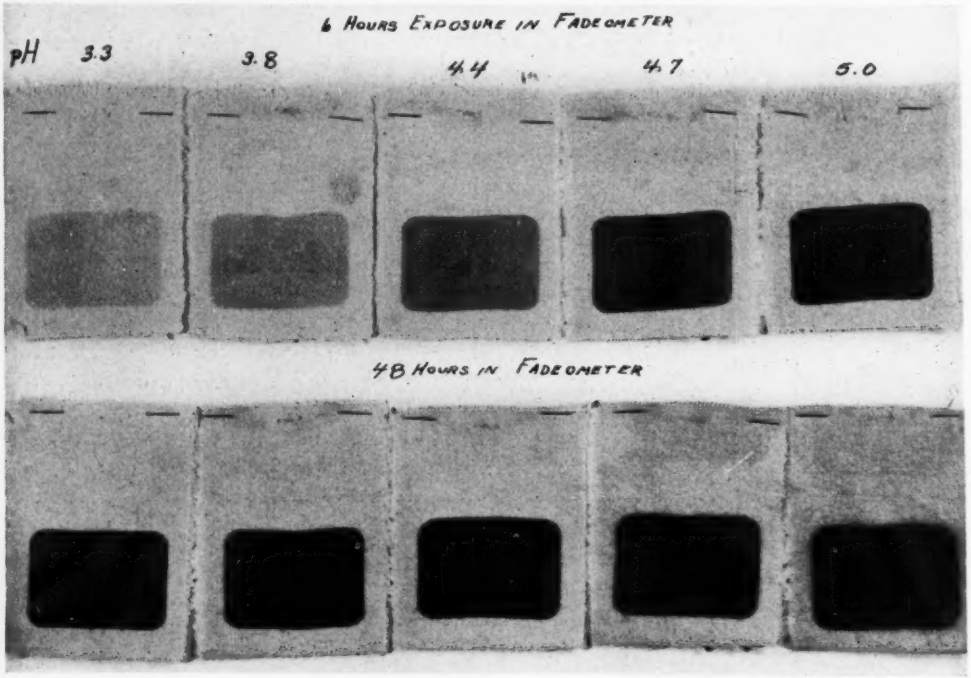


Fig. 6—Light Damage Determined by Lead Acetate.

The Determination of Sulfide Sulfur Due to Light Damage

Treat sample in 100X volume of 0.05 per cent solution of lead acetate (standardized) at pH 4.4 for 40 minutes at a boil under a reflux. Take an aliquot and titrate with standard ammonium molybdate solution using tannin as an outside indicator.

Since these samples will always be comparative, it is sufficient to standardize the lead acetate solution against the molybdate and always run a blank. Damage should be in proportion to the loss of lead from the treating solution or change in concentration.

Other metallic ions such as copper, iron, mercury, etc., have also been proposed for investigation in connection with the determination of sulfide sulfur.

ACKNOWLEDGEMENT

This investigation was made possible by a grant from the Textile Foundation to the American Association of Textile Chemists and Colorists. We wish to express our appreciation for the aid given.

We regret to state that owing to a change of policy on the part of the Textile Foundation, that is, concentration of their research projects at the National Bureau of Standards, funds for this project have been discontinued and work therefore has been stopped at this point. This paper merely constitutes a progress report covering the period for which funds were available. In the event that support for the continuance of this project becomes available, we are prepared to carry on from this point.

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A Comparison of Carbon Tetrachloride, Naphtha, and Water for the Cleaning of Cellulose-Acetate Rayon, Regenerated-Cellulose Rayon, Wool, Wild Silk, Silk, and Weighted Silks*

FLORENCE BARR, A. J. MARSHALL, and RACHEL EDGAR**

THIS comparative study of carbon tetrachloride as a cleaning agent for textiles, although not carried out as planned, is reported because of the few published data about this use of carbon tetrachloride. In 1932 Hughes and Appel stated that of the fabrics they tested, cotton, cellulose-acetate rayon, regenerated-cellulose rayon, wool, silk, and weighted silks, only the weighted silks decreased more than twenty per cent in strength during ten cleanings with carbon tetrachloride[13]. Brown found that 36 hours' treatment with carbon tetrachloride brought about no decrease in the breaking strength of cotton, linen, cellulose-acetate rayon, regenerated-cellulose rayon or silk fabrics[5]. Hale and Mack observed that silk and tin-

*Journal Paper No. J-773 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 262.
**Iowa Agricultural Experiment Station.

TABLE I

Analysis of Fabric

Fabric	Weight	Distribution of Yarns in Fabrics: By Number		By Weight		Yarn Number		Twist
		Warp	Filling	Warp	Filling	Warp	Filling	Filling
	Ounces Per Square Yard	Number Per Inch	Number Per Inch	Percentage of Fabric	Percentage of Fabric	Type	Type	Number Per Inch, Direction
1. Cellulose-acetate rayon	2.81	202	59	67.8	32.0	65.0	39.4	*
2. Regenerated-cellulose rayon	2.82	118	75	63.1	37.9	41.9	42.2	30S
3. Wool	2.82	59	59	52.2	47.4	22.9	31.9	9Z
4. Wild-silk pongee	1.61	78	61	50.7	45.7	61.9	36.1	*
5. Wild-silk shantung	7.69	77	41	26.6	72.8	26.9	3.84	*
6. Silk	2.22	246	109	59.0	40.3	127.8	88.2	60†
7. Iron-weighted silk	3.00	160	74	69.0	31.1	48.7	46.9	62†
8. Lead-weighted silk	3.23	127	74	60.6	37.8	37.4	35.4	31†
9. Tin-weighted silk	2.91	155	72	65.1	34.9	44.8	44.8	75†
10. Tin-lead-weighted silk	3.12	180	79	71.4	28.5	45.4	48.5	84†
11. Zinc-weighted silk	2.86	170	70	73.0	26.0	51.9	48.5	62†

*These filling yarns and all warp yarns but those of the wool were not measurably twisted; the wool warp yarn analyzed 9 S-twists per inch.
†Two S-twisted yarns alternated with two Z-twisted yarns in these crepes.

Analysis of Fabric (continued)

Fabric	Breaking Strength of Fabric: Conditioned		Wet		Elongation of Fabric at Breaking Load: Conditioned		Wet	
	Warp Pounds Per Inch	Filling Pounds Per Inch	Warp Pounds Per Inch	Filling Pounds Per Inch	Warp Percentage	Filling Percentage	Warp Percentage	Filling Percentage
1. Cellulose-acetate rayon	31	18	18	8	17	34	27	39
2. Regenerated-cellulose rayon	26	23	11	7	30	31	40	37
3. Wool	15	9	8	3	8	25	60	69
4. Wild-silk pongee	24	28	21	31	30	30	42	52
5. Wild-silk shantung	60	130	39	101	50	44	61	43
6. Silk	39	32	35	26	49	50	56	55
7. Iron-weighted silk	34	12	33	9	10	7	24	34
8. Lead-weighted silk	30	12	17	7	7	7	16	23
9. Tin-weighted silk	38	13	20	6	10	9	35	28
10. Tin-lead-weighted silk	42	13	24	6	10	7	35	31
11. Zinc-weighted silk	40	14	23	7	10	8	35	31

Analysis of Fabric (continued)

Fabric	Aqueous Extract	Ash		Weighting Aluminum		Iron	Lead	Phosphorus	Silica	Tin	Zinc
	% of Fabric	Warp % of Warp Yarn	Filling % of Filling Yarn	% of Fabric	% of Fabric	% of Fabric	% of Fabric	% of Fabric	% of Fabric	% of Fabric	% of Fabric
7. Iron-weighted silk	10.9	42.5	40.2	70.6		15.11		0.56	12.52		
8. Lead-weighted silk	8.8	44.5	44.6	55.3	trace		12.21	0.91	20.30		
9. Tin-weighted silk	7.2	54.2	52.9	61.3				0.45	20.49	8.80	
10. Tin-lead-weighted silk	4.4	52.6	48.7	60.8	trace		9.10	1.06	14.91	8.66	
11. Zinc-weighted silk	4.6	53.7	49.9	63.5	0.85			0.57	15.07		11.12

weighted silk suffered greater losses in strength when soap was used with carbon tetrachloride[12].

Eleven plain-woven fabrics (Table I), ten undyed (cellulose-acetate rayon faille taffeta, regenerated-cellulose rayon crepe, wool batiste, wild silk pongee, wild-silk shantung, silk crepe, lead-weighted silk crepe, tin-weighted silk crepe, tin-lead-weighted silk crepe, and zinc-weighted silk crepe) and one black iron-weighted silk crepe, have been cleaned with:

A. Carbon Tetrachloride at the National Association Institute of Dyeing and Cleaning, Inc., Silver Spring, Maryland.

A load of 1.5-yard lengths of each of the experimental fabrics and enough heavy woolens to total twenty pounds was cleaned for five minutes in a *Zoric* system containing carbon tetrachloride, drained, cleaned for thirty minutes in carbon tetrachloride containing one pint of chlorinated-solvent soap, drained, rinsed once for five minutes and three times for three minutes each in carbon tetrachloride, drained, extracted for seven minutes, and tumbled for thirty minutes at a temperature below 19° C. Through oversight no record was kept of the number of loads cleaned with soap; it has been estimated that soap was used for eighteen of the 33 loads and that soaps No. 1 (1.2 per cent oleic acid and 31.5 per cent potassium oleate), No. 2 (3.3 per cent oleic acid and 26.8 per cent sodium oleate), and No. 3 (37.5 per cent potassium oleate and 1.4 per cent material insoluble in alcohol but yielding an aqueous extract of 0.8 per cent potassium oxide) were used rather equally. After each cycle of cleaning the cloths were pressed with steam not in excess of 65 pounds.

B. Naphtha at Marshall and Swift, Inc., Mason City, Iowa.

A load of 1.5 yards of each fabric was cleaned for forty minutes in Stoddard Solvent[20], extracted, and pressed with steam. It had been planned to clean all the fabrics 33 times since similar weighted silks had withstood this number of cleanings[18] but the tin-weighted silk split at its twenty-fourth and the tin-lead-weighted silk at its twenty-ninth cleaning with naphtha.

C. Naphtha and Soap at Marshall and Swift, Inc.

A load of 1.5 yards of each fabric was cleaned for ten minutes in Stoddard Solvent, extracted, cleaned for thirty minutes in Stoddard Solvent and strong soap solution (a concentration approximately eight per cent[9]), extracted, rinsed in a continuous flow of Stoddard Solvent for twenty minutes, extracted, and pressed with steam. The tin-weighted and tin-lead-weighted silks split after ten cleanings, the iron-weighted silk after 24 and the lead-weighted silk after 29 cleanings with naphtha and soap (13.6 per cent oleic acid and 28.7 per cent potassium oleate).

D. Water and Soap in This Laboratory.

Each of the 1.5-yard lengths of cloth was washed separately by hand in fifty volumes of 0.5 per cent solution (five grams per liter of solution) of olive-oil soap (98.3 per cent anhydrous soap, 9.9 per cent combined alkali, 0.8 per cent material volatile at 105° C., titer of 12.8° C., and acid number of fat acids 197.8) in distilled water for five minutes at room temperature, rinsed in distilled water until the rinse no longer foamed, wrapped in a towel until nearly dry, and pressed with a moderately hot iron. Each fabric was laundered 33 times in this manner.

All the residual fabrics were analyzed for weight (Table II), thickness (Table III), shrinkage (Table IV), greyness (Table V), ash (Table VI), and conditioned and wet breaking strength (Tables VII and VIII); the cellulose-acetate rayon was further analyzed for acetyl, the silks and wool for nitrogen, and the wool which contained no sulfite sulfur[10] for its total and sulfate sulfur (Tables IX and X).

TABLE II
Weight Per Square Yard of Original Fabric After Cleaning

Fabric	Cleaning			
	Carbon Tetrachloride and Soap %	Naphtha %	Naphtha and Soap %	Water and Soap %
1. Cellulose-rayon acetate	99	99	98	98
2. Regenerated-cellulose rayon	94	91	94	100
3. Wool	87	87	81	102
4. Wild-silk pongee	82	78	83	76
5. Wild-silk shantung	77	75	78	72
6. Silk	95	98	93	95
7. Iron-weighted silk	87	91	80†	94
8. Lead-weighted silk	86	94	69‡	85
9. Tin-weighted silk	77	77†	78*	66
10. Tin-lead-weighted silk	77	76‡	81*	79
11. Zinc-weighted silk	81	81	65	73

*Fabric cleaned 10 times.
†Fabric cleaned 24 times.
‡Fabric cleaned 29 times.

TABLE III
Thickness of Fabric

Fabric	Cleaning				
	None 0.001 Inch	Carbon Tetrachloride and Soap 0.001 Inch	Naphtha 0.001 Inch	Naphtha and Soap 0.001 Inch	Water and Soap 0.001 Inch
1. Cellulose-acetate rayon	6.3	6.7	6.4	6.3	3.9
2. Regenerated-cellulose rayon	7.5	7.2	7.7	7.6	4.7
3. Wool	7.9	8.3	7.8	7.3	13.7
4. Wild-silk pongee	4.9	4.2	4.1	3.9	4.6
5. Wild-silk shantung	16.7	15.0	15.7	14.7	14.6
6. Silk	6.7	6.5	6.5	6.5	6.0
7. Iron-weighted silk	6.6	6.5	6.7	6.3†	6.9
8. Lead-weighted silk	6.5	5.7	5.8	4.7‡	6.9
9. Tin-weighted silk	6.3	5.4	5.1†	5.3*	5.5
10. Tin-lead-weighted silk	6.5	5.5	5.2‡	5.4*	5.8
11. Zinc-weighted silk	6.2	6.0	5.9	4.9	4.8

*Fabric cleaned 10 times. †Fabric cleaned 24 times. ‡Fabric cleaned 29 times.

TABLE IV
Shrinkage of Fabric

Fabric	Shrinkage of Warp — Cleaning: Carbon Tetrachloride and Soap %	Naphtha %	Naphtha and Soap %	Water and Soap %	Shrinkage of Filling — Cleaning: Carbon Tetrachloride and Soap %	Naphtha %	Naphtha and Soap %	Water and Soap %
1. Cellulose-acetate rayon	1	1	1	1	3	5	5	5
2. Regenerated-cellulose rayon	2	2	3	0	5	8	7	*4*§
3. Wool	7	10	8	36	7	7	7	*37*
4. Wild-silk pongee	0	3	5	2	*1*	0	1	3
5. Wild-silk shantung	5	8	8	7	7	7	7	0
6. Silk	0	0	1	0	*2*	0	3	*7*
7. Iron-weighted silk	10	10	10†	19	*3*	*3*	*3*†	*3*
8. Lead-weighted silk	5	4	6‡	16	*4*	*5*	*1*‡	*1*
9. Tin-weighted silk	0	*1*†	*1**	6	6	4†	6*	6
10. Tin-lead-weighted silk	4	4‡	3*	11	0	0‡	*1**	1
11. Zinc-weighted silk	5	4	5	11	4	3	3	1

*Fabric cleaned 10 times. †Fabric cleaned 24 times. ‡Fabric cleaned 29 times. §Numbers in italics refer to stretch.

TABLE V
Greyness of Fabric

Fabric	Cleaning: None Percentage of Light Absorbed	Carbon Tetrachloride and Soap Percentage of Light Absorbed	Naphtha Percentage of Light Absorbed	Naphtha and Soap Percentage of Light Absorbed	Water and Soap Percentage of Light Absorbed
1. Cellulose-acetate rayon	11	37	24	26	22
2. Regenerated-cellulose rayon	16	34	28	27	15
3. Wool	27	36	34	28	36
4. Wild-silk pongee	29	38	36	37	46
5. Wild-silk shantung	25	39	33	34	37
6. Silk	15	26	24	24	23
8. Lead-weighted silk	22	30	28	33‡	23
9. Tin-weighted silk	14	19	21†	21*	18
10. Tin-lead-weighted silk	22	20	27‡	22*	18
11. Zinc-weighted silk	19	21	23	29	23

*Fabric cleaned 10 times. ‡Fabric cleaned 29 times. †Fabric cleaned 24 times.

TABLE VI
Ash of Fabric

Fabric	Cleaning: None Percentage of Fabric	Carbon Tetrachloride and Soap Percentage of Fabric	Naphtha Percentage of Fabric	Naphtha and Soap Percentage of Fabric	Water and Soap Percentage of Fabric
1. Cellulose-acetate rayon	0.1	0.4	0.3	0.3	0.1
2. Regenerated-cellulose rayon	0.2	1.7	0.9	2.0	0.2
3. Wool	0.5	0.8	0.9	0.9	1.1
4. Wild-silk pongee	0.1	0.8	1.0	1.1	1.1
5. Wild-silk shantung	28.0	15.1	16.8	12.2	12.8
6. Silk	0.3	0.5	0.5	0.5	0.5
7. Iron-weighted silk	43.7	42.5	43.1	42.2†	45.5
8. Lead-weighted silk	44.2	42.4	42.8	40.5‡	44.6
9. Tin-weighted silk	52.9	49.4	51.0†	49.7*	50.4
10. Tin-lead-weighted silk	50.3	50.1	50.2‡	50.0*	50.3
11. Zinc-weighted silk	51.9	47.0	46.9	47.3	47.4

*Fabric cleaned 10 times. †Fabric cleaned 24 times. ‡Fabric cleaned 29 times.

TABLE VII
Conditioned Breaking Strength of Fabric as Percentage of Original Conditioned Strength

	Warp Strength — Cleaning: Carbon Tetrachloride and Soap	Naphtha	Naphtha and Soap	Water and Soap	Filling Strength — Cleaning: Carbon Tetrachloride and Soap	Naphtha	Naphtha and Soap	Water and Soap
1. Cellulose-acetate rayon	93	93	87	73	68	68	61	68
2. Regenerated-cellulose rayon	105	100	91	55	87	87	94	90
3. Wool	96	92	88	76	93	93	67	73
4. Wild-silk pongee	74	71	32	48	89	65	50	74
5. Wild-silk shantung	68	60	44	63	81	84	59	72
6. Silk	94	88	75	81	107	80	50	70
7. Iron-weighted silk	86	57	57†	52	81	81	19†	63
8. Lead-weighted silk	71	67	4‡	33	69	69	6‡	63
9. Tin-weighted silk	60	48†	56*	24	‡	6†	50*	6
10. Tin-lead-weighted silk	48	13‡	52*	11	16	6‡	§	31
11. Zinc-weighted silk	83	52	35	22	55	55	§	20

*Fabric cleaned 10 times. †Fabric cleaned 24 times. ‡Fabric cleaned 29 times. §Cleaned fabric of no measurable strength.

TABLE VIII

Wet Breaking Strength of Fabric as Percentage of Original Conditioned Strength

Fabric	Warp Strength					Filling Strength				
	Cleaning					Cleaning				
	None	Carbon Tetrachloride and Soap	Naphtha	Naphtha and Soap	Water and Soap	None	Carbon Tetrachloride and Soap	Naphtha	Naphtha and Soap	Water and Soap
1. Cellulose-acetate rayon	60	53	47	47	40	45	23	32	19	42
2. Regenerated-cellulose rayon	41	36	32	32	32	29	26	23	19	35
3. Wool	56	56	48	36	36	33	40	40	20	40
4. Wild-silk pongee	87	52	48	19	19	111	74	59	43	22
5. Wild-silk shantung	65	59	51	38	37	78	66	63	53	56
6. Silk	88	81	69	50	50	80	73	57	27	60
7. Iron-weighted silk	100	71	52	43†	43	75	50	63	19†	38
8. Lead-weighted silk	54	25	33	4‡	16	56	25	38	6‡	6
9. Tin-weighted silk	52	28	24†	24*	8	44	6	6†	28*	6
10. Tin-lead-weighted silk	56	13	13‡	22*	4	50	§	6‡	§	§
11. Zinc-weighted silk	61	26	22	9	9	50	25	30	§	§

*Fabric cleaned 10 times. †Fabric cleaned 24 times. ‡Fabric cleaned 29 times. §Cleaned fabric of no measurable wet strength.

TABLE IX

Silk Content of Loaded and Weighted Fabrics

Fabric	Cleaning				
	None Percentage of Fabric	Carbon Tetrachloride and Soap Percentage of Fabric	Naphtha Percentage of Fabric	Naphtha and Soap Percentage of Fabric	Water and Soap Percentage of Fabric
4. Wild-silk pongee	78.9	97.7	97.9	98.4	99.6
5. Wild-silk shantung	65.4	85.6	85.4	84.3	89.6
7. Iron-weighted silk	43.9	45.3	46.1	44.6†	43.1
8. Lead-weighted silk	49.3	46.9	47.1	47.2‡	51.1
9. Tin-weighted silk	49.8	44.9	45.5†	45.9*	45.4
10. Tin-lead-weighted silk	45.5	43.2	43.9‡	43.8*	45.3
11. Zinc-weighted silk	43.6	46.0	46.2	45.6	47.9

*Fabric cleaned 10 times. †Fabric cleaned 24 times. ‡Fabric cleaned 29 times.

TABLE X

Effect of Cleaning Upon the Acetyl Content of Cellulose-Acetate Rayon, the Nitrogen of Silk, and the Nitrogen and Sulfur of Wool

Cleaning	Acetyl of Cellulose-Acetate Rayon Percentage of Fabric	[redacted] Nitrogen of Silk Percentage of Fabric	Nitrogen of Wool Percentage of Fabric	Sulfur of Wool		
				Total Percentage of Fabric	Sulfate Percentage of Fabric	Non-Sulfate Percentage of Fabric
None	39.1	18.59	16.50	4.69	0.73	3.96
A. Carbon tetrachloride and soap	39.0	18.62	16.32	4.65	0.69	3.96
B. Naphtha	38.9	18.66	16.33	4.68	0.63	4.05
C. Naphtha and soap	38.9	18.60	16.25	4.56	0.72	3.84
D. Water and soap	39.2	18.66	16.29	4.08	0.15	3.93

In general these quantitative data describe the cleaning with carbon tetrachloride and soap as least degrading to the fabrics and the cleaning with naphtha and soap as the most degrading, although fabrics cleaned by the latter method were much less greyed.

METHODS OF ANALYSIS

Acetyl. Values for acetyl are the means of three parallel determinations with dried two-gram samples[7].

Ash. A three-gram sample of fabric, brought to constant weight at 105° to 110° C. in a weighing bottle by the method of tares, was transferred to a crucible and ignited to constant weight in an electric muffle furnace at dull red heat; mean values for ash have been computed from three parallel determinations.

Breaking Strength of Fabric and Elongation at Breaking Load. Twenty warp samples of each new and cleaned fabric were cut 1.5 inches wide and six inches in the warp direction, no sample nearer the selvage than one-tenth the width of the fabric, and no two samples including the same warp yarns; these samples were raveled accurately to a width of one inch by taking nearly the same number of warp yarns from either edge. Filling samples were similarly prepared and ten warp and ten filling samples from each fabric were conditioned at 65 ± 2 per cent R.H. and 20 ± 2° C. for a week before testing; the other samples were immersed in distilled water for one hour before testing. All the strengths were determined within two days and with a *Scott Universal Tester* whose lower jaw, clamped in the sample three inches below the upper jaw, traveled at a rate of twelve inches per minute. Mean strength per yarn was calculated from ten determinations and used for computing change in strength upon cleaning. Elongation at breaking load was measured to one-ninth inch on an autographically recorded stress-strain curve[2].

Distribution of Yarns by Number. The number of warp yarns per inch of each new and cleaned fabric was counted with a thread counter in five places within the fabric of which none was nearer the selvage than one-tenth the width of the fabric and no two included the same yarns; number of filling yarns per inch was similarly de-

termined[2]. Warp shrinkage was computed from change in number of filling yarns per inch of fabric and filling shrinkage from change in number of warp yarns.

Distribution of Yarns by Weight. Two two-inch squares of each new fabric were cut no nearer the selvage than one-tenth the width of the fabric, conditioned for a week, separately weighed to the nearest milligram, and raveled into constituent yarns; all the warp yarns from a square were weighed together to the nearest milligram and weight of filling yarns was determined in the same way.

Greyness of Fabric. Absorption of light by fabric was read with a Pfaltz and *Bauer Reflectometer Universal Model MU* using a voltage of 3.8 and a lamp for an hour. With photocell insert on the white standard the pointer of the microammeter was set on zero of the scale by means of the regulating resistances; with photocell insert on the black standard the pointer was set on 100 by adjustment of the sensitivity regulator and resetting and readjustment were continued until the pointer showed zero on the white and 100 on the black without adjustment. Several thicknesses of cloth were clamped tightly in a frame for photometric reading; the mean of five determinations has been reported as the absorption of light.

Nitrogen. Mean values for total nitrogen of silk and wild silks[11], weighed silks[15], and wool[8] have been computed from three parallel determinations according to Kjeldahl methods using three-gram samples dried to constant weight. Factors of 5.379 and 5.479 have been used, respectively, to convert values for nitrogen into those for silk fibroin and wild-silk fibroin.

Soaps. The chlorinated-solvent soaps were analyzed for oleic acid and soap according to Marshall's method[16]; the residue from distillation of a weighed 25-milliliter sample was dissolved in petroleum ether, evaporated, dissolved in alcohol, titrated with alcoholic alkali until neutral to phenolphthalein, dissolved in water, and titrated with hydrochloric acid until neutral to methyl orange. The values reported are the means of three parallel determinations. The other drycleaning soap was similarly analyzed from smaller air-dry samples and the olive-oil soap was analyzed according to standard methods[19, 3].

Sulfur. Values for total sulfur of wool are the means of three parallel determinations, with dried three-gram samples according to the Benedict-Denis method[4, 6, 3]. Values for the wool's sulfate sulfur are the means of two parallel determinations with dried two-gram samples according to Mease's method[17].

Thickness of Fabric. Ten measurements of thickness were made at different places in the fabric, exclusive of cloth within six inches of selvage, with a micrometer which pressed on a circle of cloth three-eighths inch in diameter with a pressure of six ounces[1].

Twist of Yarn. A yarn was removed from the fabric for a distance of ten inches, at this point gripped in the right clamp of an *Improved United States Testing Company Tester* and clipped 0.5 inch to its right before removal from fabric for fifteen inches and, with locking bar open pulled under tension (load in grams equal to 131/typp) in the left clamp until the index pointer came in line with the starting mark, tightened in the clamp, and clipped 0.5 inch to its left. The clamps were set four inches apart for wool yarns and at ten inches for other yarns; the right clamp was rotated until all twist was removed from the yarn. Mean twist per inch of yarn was computed from ten determinations and a yarn described as of S twist if, when held vertically, its spirals conformed in slope to the central portion of the letter S, and as of Z twist if the spirals slanted as the middle line of Z[2].

Weight of Fabric. Three samples, four inches long and the entire width of fabric, were cut from each new and cleaned cloth, conditioned for a week, and weighed to the nearest milligram. Each sample was then laid without tension on a flat horizontal and measured to a thirty-secondth of an inch in five places parallel to selvage[2]. Mean width of new fabric was computed from five measurements and mean width of cleaned fabric from width of new fabric and numbers of warp yarns per inch in new and cleaned fabric.

Yarn Number. Two ten-yard or longer lengths of warp yarn from each new cloth were measured, wrapped on a card, conditioned for a week, removed from the card, and separately weighed to the nearest milligram; weight of filling yarn was determined in the same way.

A part of the analyses of the new silk and weighted silks has been reported before[14].

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OBITUARY

ARTHUR A. STEWART

ARTHUR A. STEWART, member of the Lowell Textile Institute faculty for 40 years, died on Thursday, October 3rd, at his home in Lowell after an illness of five months.

Prof. Stewart was a native of Montreal, Canada, and came to Lowell at an early age. He graduated from Lowell Textile with the class of 1900. In the fall of that year he was appointed to the faculty and later was made head of the textile finishing department.

He was active in banking circles, being president of the Lowell Cooperative Bank and a member of the corporation of the Merrimac Savings bank. He was secretary and treasurer of the Lowell Textile Alumni Association and a charter member of Omicron Pi fraternity. He was also a member of the Yorick club.

Prof. Stewart was an active member of the Masonic order for many years holding the position of right eminent grand commander of the Grand Commandery, Knights Templar, of Massachusetts and Rhode Island at the time of his death.

He is survived by his widow, a son and a sister.

• GENERAL RELEASE

General Dyestuff Corp., 435 Hudson Street, New York City, announces release of a circular describing the following product:—

Indanthrene Black Brown V A Paste—a straight vat color which is recommended by the manufacturers for the dyeing of cotton, rayon, and linen in their various forms. It is best dyed according to the I W process. It is said to possess very good fastness to light, washing and chlorine. It is especially suited for the production of chocolate brown shades on yarns and, according to the pigment padding method, on cotton piece goods. It is stated that, due to its good solubility, it can satisfactorily be used in package machines and is well adapted also for piece dyeing according to the continuous dyeing method.

• JOINS NATIONAL STARCH

William L. Pierce, for the past 20 years connected in an executive capacity with the Bellman Brook Bleachery of Fairview, N. J., and the Newburgh Bleachery, Newburgh, N. Y., has joined the Textile Division of National Starch Products Inc. Mr. Pierce is active in various textile associations and has numerous friends connected with the industry.

"Miss America, 1940"

• MISS AMERICA IN SCHOLLER ADVERTISING

Miss Frances Burke, "Miss America, 1940," was selected in July for two of the current series of photographs used in Scholler Bros., Inc., *DuraBeau* advertising. First of these was used in September; the other appears in a December issue of American Dyestuff Reporter.

Up until the time of her choice as "Miss America," Miss Burke, a newcomer as a photographic model, is reported to have posed for but four advertising illustrations—and two of these were for *DuraBeau* advertising.

Photographs were made under the direction of the R. E. Lovekin Corporation, Advertising Agency for Scholler Bros., Inc.

• ANNUAL MEETING, U.S.I.T.R.

The eleventh annual meeting of U. S. Institute for Textile Research will be held on Thursday, November 14, at the Hotel Pennsylvania, New York City. The program as tentatively arranged by the Board of Directors at their recent meeting in New York, calls for a morning session, starting at 11 A.M. for the presentation of annual reports and other routine business, this to be followed by a luncheon open to members and guests, while the afternoon will be devoted to conferences on two important new research projects.

One of the latter relates to a proposed extension of the completed research on textile drying to cover certain subjects more exhaustively than has been possible thus far.

At the other conference there will be presented for discussion and acceptance after possible revision the tentative program for the research on Effects of Processing on the Wool Fiber, which program has been prepared by the Committee appointed following the conference on this subject at the last annual meeting.

The tentative program for this research has been approved by the Research Council and the Board of Directors, and the Council has approved the appointment of the program committee as the Administration Committee for the research, as follows: Rinaldo A. Lukens, Continental Mills, Inc., Philadelphia, Pa., Chairman; Dr. Werner Von Bergen, Forstmann Woolen Co., Passaic, N. J.; Hugh Christison, Arlington Mills, Lawrence, Mass.; Dr. Milton Harris, Research Director, Textile Foundation, National Bureau of Standards, Washington, D. C.; Dr. A. C. Walker, Bell Telephone Laboratories, New York, N. Y.; E. D. Walen, Pacific Mills Worsted Division, Lawrence, Mass.

As is always the case when the Institute has a new research subject to discuss or a research project to organize, they are presented at conferences open to all who are interested, irrespective of whether or not they are Institute members. Therefore, a cordial invitation is extended to all connected with the textile industry, and to others who may be interested to attend the conferences and also the luncheon.

For copies of the tentative program on Effects of Processing on the Wool Fiber and for program of the meeting address C. H. Clark, Secretary, 65 Franklin Street, Boston, Massachusetts.

The following committees will act in connection with the annual meeting:

Committee on Nominations—Earl Constantine, Chairman; Arthur Besse, Ephraim Freedman, Douglas G. Woolf.

Burget Committee—Dr. H. DeWitt Smith, Chairman; Dr. F. Bonnet, Dr. A. C. Walker, W. D. Appel.

• MICHIGAN ALKALI GOLDEN JUBILEE

The golden jubilee anniversary of the Michigan Alkali Company, founded in 1890 by the late Capt. John Baptiste Ford, was celebrated Thursday night (Oct. 17) at a banquet honoring 567 employes who have been with the company a quarter century or longer. The affair was held at the company's clubhouse.

Officials of the company, most of them direct descendants of the old Captain, presented gold watches to the entire list of honor guests as token awards for their long service. Among those presenting the gifts was Emory L. Ford, president of the

company, and John B. Ford, Jr., vice president.

Captain Ford, one of the most colorful figures in American industrial history and father of the plate glass manufacturing in this country, founded Michigan Alkali as the crowning achievement of his long career. He was 79 years old at the time and lived until May, 1903. His sons, grandsons and great grandsons have carried on since then, with the alkali establishment becoming one of the largest and most important chemical companies in the nation.

Wyandotte was chosen as the company site by the captain when he found that immense salt beds in the ground underneath this strategic Detroit River community could be utilized in the manufacture of soda ash, an important ingredient of glass. Captain Ford at the time was part owner of the Pittsburgh Plate Glass Company.

The oldest employe honored Thursday night was John A. Wolcott, 77. He went to work for the old captain in 1891, a year after Michigan Alkali was founded, and has been with the company continuously since them. He now is master mechanic.

Oldest of the women employes to receive the award was Miss May Milkins, who served the company for 31 years as telephone operator.

Fifty-two of the employes on the honor list have been with the company for more than 40 years.

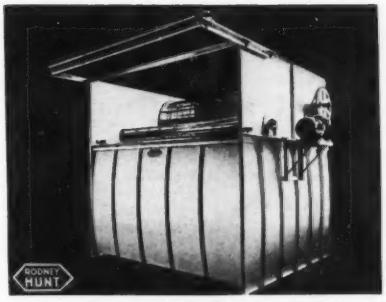
Prior to the banquet, a new flagpole erected in front of the Michigan Alkali Company's office building was dedicated. A flag was presented to John B. Ford, Jr., by the Veterans of Foreign Wars Post No. 1136. The Dearborn VFW post drum and bugle corps participated in the dedication ceremonies.

• NEW YARN CONDITIONING AGENT

The Burkart-Schier Chemical Company of Chattanooga, Tennessee has perfected a new conditioning fluid, Tenesol, for cotton textile yarns. Used in dilute solution in water, its rapid wetting action is said to afford a complete moisture regain in a minimum of time. Due to the hygroscopic nature of this product, there is excellent retention of the regain.

This yarn conditioning agent may be used in all types of conditioning and twist-setting machines. Yarns conditioned with this fluid are said to show an even penetration and absorption of moisture, with no surface globules, or droplets of water. Because the twist is permanently set, weaving is greatly facilitated. It is stated that there is absolutely no harmful action upon the fiber, and no interference with subsequent dyeing and finishing operations.

Tenesol is said to be inexpensive to use. One gallon per hundred gallons of water is recommended. Sample and booklet will be furnished on request.



"Tru-Shade" Dye Kettle

• MODERNIZES DYE-HOUSE

The Artloom Corporation of Philadelphia has recently completely modernized their dye-house with "Tru-Shade" stainless steel dyeing machines purchased from the Rodney Hunt Machine Company of Orange, Massachusetts.

It is stated that these new stainless steel units have replaced wood dye kettles and will bring greatly increased speed and ease of production. The new machines are said to permit the changing of dye shades easily and make possible a uniform matching of material. This is of special importance in the case of the Artloom Corporation where they manufacture large quantities of fabric for automobiles and where it is essential to have identical shades in piecing goods to make upholstery and car linings. In the photograph, note the curved sides of the machines—a patented feature of the new "Tru-Shade" Machines which the Rodney Hunt Company claims gives added strength and long life to the equipment, being preformed along hydro-dynamic principles to prevent the flexing of the tub sides when the dye liquor is introduced or removed.

• CALCO RELEASES

The Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J., has released bulletins on the following products:—

Calcomine Chrome Brown BS—According to the bulletin, dyers of uncarbonized, reworked wool will find it produces full brown shades of satisfactory fastness to light and fulling. Incidental fibers of cotton, viscose rayon and silk will be well covered.

Calcocid Yellow MCG (C. I. No. 640)—a level, sulfuric acid dye producing a bright shade yellow with a green tone. This dyestuff is recommended by the manufacturers for hat bodies, carpet yarns, curtain and tapestry fabrics, mohair and also for knitting yarns. It is applied in the usual method for sulfuric acid colors. It is stated that, for reasons of economy, wool dyers will be interested in this color.

Copies of these bulletins, giving complete property tables and dye procedures, can be obtained from Calco at Bound Brook, New Jersey.

• POLYVINYL ACETATES

Facts concerning polyvinyl acetates, the thermoplastic resins produced by the Du Pont Company, are contained in a technical bulletin just issued by The R. & H. Chemicals Department of that Company. Information concerning different grades and specific applications is given. The bulletin also contains a discussion of the uses of polyvinyl acetates in various industries. Copies may be had on application to The R. & H. Chemicals Department of E. I. du Pont de Nemours & Company, Wilmington, Delaware.

• NOPCO DIVISIONS MERGER

T. A. Printon, Vice President of National Oil Products Company, announces the merging of the Laundry Division with Division H of the Industrial Sales Department. In charge of the sales of this division will be Marvin S. Eavenson. Mr. Eavenson, a graduate of the University of Pennsylvania, was for years connected with Colgate and Company, and later with the Colgate-Palmolive-Peet Company, as divisional sales manager. He is said to bring to his new position a large acquaintance in the trade and a wealth of merchandising experience.

• MEETING, A.A.T.T.

The November meeting of the American Association of Textile Technologists will be held at the Architectural League, 115 East 40th St., New York City, on Wednesday, November 6th, at 6:00 P.M. The speaker will be Dr. Harold DeW. Smith of A. M. Tenney Associates, Inc., whose subject will be "Fiber Mechanics." Reservations for the meeting should be made with the secretary, Miss Bernice S. Bronner, Good Housekeeping Institute, 57th St. and 8th Ave., New York City.

• "MODINAL" D

A new concentrated detergent, "Modinal" D, is announced by the Gardinol Corporation, Wilmington, Delaware. The strength of the product, greater than that of "Modinal" ES, will permit economies which will broaden its use, the company says.

The new detergent, almost equally efficient in hard and soft water, is a wetting and penetrating agent, dyeing assistant and general all around surface active agent, according to the company. It is recommended for all fibers.

Sales agents for the detergent are Procter & Gamble, Cincinnati, Ohio, and E. I. du Pont de Nemours & Company, Wilmington, Del.

• INSPECTORS SOUGHT FOR ARMY

Inspectors of miscellaneous supplies are needed by the Quartermaster Corps of

the War Department in connection with the National Defense program. The Civil Service Commission is, therefore, receiving applications to fill the following positions: Inspector of hats, $2,000 a year; inspector of miscellaneous supplies (hosiery and knit underwear), $2,000 a year; inspector of textiles, $2,000 a year; junior inspector of textiles, $1,620 a year; inspector of clothing, $2,000 a year; junior inpector of clothing, $1,620 a year. The salaries are subject to a 3½ per cent retirement deduction.

Hat inspectors must have had general experience in manufacturing and supervising the manufacturing of fur-felt hats or inspecting felt hats in connection with purchases in wholesale lots; miscellaneous supplies inspectors must have had experience in a hosiery or knitted underwear manufacturing establishment in inspecting these supplies or in supervising the manufacturing processes; inspectors of textiles must have had broad experience in the textile industry in designing textiles or in other textile-mill operations, except that a course in a textile school may be substituted for part of the experience. Inspectors of clothing must have had preliminary experience in the clothing manufacturing business which would render the applicant familiar with materials and processes used in men's outer garment manufacture, and experience in inspecting clothing to determine compliance with specifications or supervisory work in connection with the manufacturing processes.

Persons who can meet these requirements are urged to file their applications with the Commission at once. Applications will be rated as received at the Commission's Washington office until further notice. No written examination is to be given. Applicants will be rated on their qualifications as shown in their applications and on corroborative evidence.

Further information regarding the requirements for these positions and the proper application forms may be obtained from the Secretary of the Board of U. S. Civil Service Examiners at any first- or second-class post office or from the U. S. Civil Service Commission, Washington, D. C.

• WARWICK ADDITIONS

Ernest Nathan, President of the Warwick Chemical Company, announces that extensive additions and improvements are under construction at their Rock Hill, S. C. plant to cope with increased business.

• SECOND NYLON PLANT

A second plant for the manufacture of nylon yarn, Du Pont's new contribution to the textile industry, will be built at Martinsville, Va., the company announced recently.

Work is to begin at once. The completed plant, it was said, will employ about 750 persons. An expenditure of approximately $11,000,000 is planned in the present development.

The plant is expected to come into production late in 1941, and be in full operation in the Spring of 1942. With facilities already in operation or under construction at Seaford, Del., site of the company's present nylon plant, it is hoped that the Martinsville project will create an aggregate capacity of approximately 16,000,000 pounds, said Du Pont officials.

The combined capacities of the two plants will be more than five times the output of nylon yarn originally contemplated when the first Seaford plant was authorized late in 1938.

A company spokesman placed the aggregate investment now made or authorized for nylon manufacture at $28,000,000. He added that no other new Du Pont product has been so heavily backed by the company in so short a time.

"Nylon yarn was introduced commercially in very limited quantities only nine months ago," said a company statement. "It reached the public in the form of women's sheer hosiery in May, while it was not until the latter part of August that the first Seaford plant attained full production.

"However, in this short period public demand for nylon hosiery and other finished products has exceeded the available rate of supply and a further expansion of manufacturing capacity is justified.

"Among other reasons, Martinsville, Va. was chosen for the site of a second nylon operation because of its proximity to the textile industry in the South. So far as is possible, workmen for the new plant will be recruited in the vicinity.

"Following its established practice, the Du Pont Company will furnish the nylon yarn to textile mills for manufacture into finished goods, and will not itself engage in this field."

Nylon yarn is now being used in men's as well as women's hosiery, and also in women's undergarments and other woven and knitted textile fabrics. Nylon fishing lines, sewing thread and surgical sutures have been on the market for some time. Monofilaments of nylon are being used widely in the manufacture of toilet and industrial brushes. However, more than 90 per cent of the nylon produced today continues to go into women's full-fashioned hosiery.

• CALIHAN TRANSFERRED

William W. Calihan, former district manager at Rochester, N. Y., for H. K. Porter Co., Inc., has been transferred to Pittsburgh to handle sales of the process equipment division, it was announced recently by T. M. Evans, president. He will make his headquarters in Pittsburgh. In addition to industrial locomotives, the Porter Company manufactures an extensive line of equipment for chemical process and related industries.

• CLASSIFIED ADVERTISEMENTS •

DYER OF WORSTEDS: 15 years' experience—7 years in charge of dyeing and blending of raw stock and slubbing for men's wear. Has been singularly successful on Government shirtings, suitings and blankets and production. References. Write Box No. 264, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED—by Dyestuff Manufacturer. Sales Manager for Southern territory. Must be familiar with the trade, know colors and textile specialties and their application. State in detail experience, age, salary expected, etc. Reply to Box No. 265, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

OPPORTUNITY WANTED: Chemist Technician thoroughly experienced in dyeing and finishing, desires an opportunity to demonstrate ability with progressive Finishing Plant. Ten years experience with outstanding concerns. Thoroughly experienced in processing of lastex swim suitings and corset goods. Can install latest methods or adapt your equipment for best results obtainable. Likes to co-ordinate or reorganize outmoded processes to meet mass-production requirements. Supervise laboratory control and research with resulting economy in dyeing and finishing. References. Write Box 262, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.